HEAT

AND THE PRINCIPLES OF THERMODYNAMICS

BY

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PREFACE

Since the first edition of this book appeared, eighteen years ago, considerable advances have been made in our knowedge of the subject, new methods of investigation have been introduced, and the relative importance of different parts of it have changed. The use of electrical appliances has extended the range and accuracy of thermometry. Means of attaining, maintaining, and measuring temperatures, which twenty years ago were somewhat crude and uncertain, have been perfected, and are employed in many operations of the heat laboratory. The measurement of heat energy is now often effected by measurements of electrical energy.

The demands made on students have correspondingly changed and increased.

The author has therefore taken the opportunity afforded him to revise the whole book in the light of these considerations. Some paragraphs of an elementary nature have been omitted, others have been abbreviated, and greater space has been given to thermometry and to electrical methods generally; but no material change has been made in the general plan of the work. The first part contains an account of the chief experimental phenomena that result from the application of heat to matter, and it is necessary that the students should themselves perform the measurements set out in this part of the book. Though laboratory instructions are not given in detail it is hoped that the operations are sufficiently indicated and the methods made

clear. The second part of the book is devoted to the consideration of heat as a form of energy, and is necessarily more mathematical. Here a slight use has been made of calculus methods; but it is now recognized that students who get sufficiently far in their science studies to deal seriously with such subjects should have some knowledge of the calculus. Numerical examples have, however, been freely introduced in order that the vague impression left in the minds of some students by general symbols may thereby be rendered more actual and precise.

The author hopes that the changes made may render the book useful to a new generation of students. His thanks are due, and are here tendered, to those who kindly called his attention to obscurities and mistakes in the previous editions, to Dr. W. F. G. Swann for reading the proofs and making suggestions, and to the Cambridge Scientific Company for permission to reproduce figures of some of their apparatus.

C. H. D.

September, 1911.

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UNITS OF MEASUREMENT

In physical science there are three fundamental ideas—those of space, matter, and time.

To express any quantity numerically we employ (i) a unit of the same kind as the quantity with which we are concerned; (ii) a number which indicates how many such units the given magnitude contains. Thus every expression of a measured quantity consists of a denominational part and a numerical part, and the magnitude of the numerical factor varies inversely as the magnitude of the unit or denominational factor.

Two system of units are used in this country—the British system, based on the foot, the pound, and the second; and the C.G.S. (centimetre-gramme-second) system. The latter is in universal use throughout Europe, and is now ordinarily employed in physical laboratories everywhere.

Multiples and sub-multiples of all the C.G.S. units are expressed by the prefixes—

Deca = 10.	Deci = $\frac{1}{10}$.
Hecto = 100.	Centi = $\frac{1}{100}$.
Kilo = 1000.	Milli = $\frac{1}{1000}$.

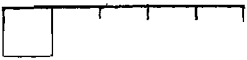
Unit of Time.—The unit of time generally used in physical science is the **second**, based on a natural unit that may be regarded as constant. Periods of time are expressed in multiples of this unit.

Unit of Length.—The unit of length is chosen arbitrarily, although it may approximate to some natural constant.

The *British* unit of length employed in physical science is the **foot**. It is one-third of the standard yard, which is defined as the distance between the centres of two lines engraved on a brass bar kept in the Exchequer Office in London.

The *C.G.S.* unit of length is the **centimetre**. It is the one-hundredth part of the standard metre, which is the length of the standard rod kept in the archives at Paris.

A length of five centimetres is shown in the accompanying figure.



The length from which the centimetre is derived is the *metre*, which is intended to represent the ten-millionth part of the distance from the pole of the earth to the equator.

The multiples and sub-multiples of the centimetre are:—

1 millimetre	= $\frac{1}{1000}$ metre (1 mm.)	=	·03937 in.
1 centimetre	= $\frac{1}{100}$ metre (1 cm.)	=	·3937 in.
1 decimetre	= $\frac{1}{10}$ metre (1 dm.)	=	3·937 in.
1 metre		=	39·37 in.
1 decametre	= 10 metres	=	32·808 ft.
1 hectometre	= 100 metres	=	109·36 yd.
1 kilometre	= 1000 metres	=	1093·6 yd.

For rough work one centimetre may be taken as $\frac{2}{5}$ in.

Unit of Area.—The C.G.S. unit of area is the square centimetre shown above.

The only magnitudes in common use in physics are the following:—

1 sq. mm.	= $\frac{1}{100}$ sq. cm.	=	·00155 sq. in.
1 sq. cm.		=	·155 sq. in.
1 sq. dm.	= 100 sq. cm.	=	15·5 sq. in.
1 sq. m.	= 10,000 sq. cm.	=	10·764 sq. ft.

Unit of Volume.—The C.G.S. unit of volume is the cubic centimetre. The magnitudes in common use in physics are:—

1 cub. mm.	= $\frac{1}{1000}$ cub. cm.	=	·000061027 cub. in.
1 cub. cm.		=	·061027 cub. in.
1 cub. dm. (called 1 litre)	= 1000 cub. cm.	=	61·027 cub. in.

Mass.—Mass means quantity of matter.

The student should learn to distinguish between mass and weight, and to think and speak of masses without regard to their weights. This is rather difficult at first, because practically we nearly always compare masses by comparing their weights. But when one takes a pound of water, for instance, what is wanted is a certain quantity of water; it is of no importance for most purposes how much it may weigh. The mass of a given lump of matter is a constant unalterable quantity, having the same value in London as on the planet Jupiter, or midway between the sun and Sirius; whereas its weight is a mere accident of its position, and would be very different indeed in these three cases. Again, if a cannon ball strike a target, the magnitude

of the effect certainly depends on the mass of the bullet, but not in the least on its weight. The effect would be the same if the earth were absent and both bullet and target weighed nothing.

Unit of Mass.—The British unit of mass is the **pound**: it is the quantity of matter contained in a lump of platinum kept at the Exchequer Office in London.

The C.G.S. unit of mass is the **gramme**. It is the thousandth part of the mass of a lump of platinum kept at Paris. It is equal to the quantity of matter contained in *a cubic centimetre of pure water* at 4° C., and it is this circumstance which constitutes its great valne as a unit.

The multiples in common use are:—

1 mg.	= $\frac{1}{1000}$ grm.	=	·01543 grain.
1 cg.	= $\frac{1}{100}$ grm.	=	·1543 grain.
1 dg.	= $\frac{1}{10}$ grm.	=	·003537 oz.
1 grm.		=	·002204 lb.
1 Kg.	= 1000 grm.	=	2·204 lb.

Conversion of British into C.G.S. Units.

1 in.	=	2·5399 cm.
1 sq. in.	=	6·451 sq. cm.
1 cub. in.	=	16·386 cub. cm.
1 ft.	=	30·4795 cm.
1 sq. ft.	=	929 sq. cm.
1 cub. ft.	=	28·315 cub. dm.
1 cub. yd.	=	·7645 cub. m.
1 oz.	=	28·349 grm.
1 lb.	=	453·59 grm.
1 poundal	=	13825 dynes.
1 ft.-pound	=	13825 grm.-cm.
1 horse-power	=	7·604 × 10^6 gr.-cm. per second.

SYMBOLS

Throughout the book the following expressions are used in a special sense:—

α = coefficient of expansion of gases.
β = the ratio between total and internal energy.
C = strength of electrical current.
C_v = the specific heat of a gas at constant volume in units of heat.
C_p = the specific heat of a gas at constant pressure in units of heat.
ϵ = elasticity.
f = force.
g = value of acceleration due to gravity.
H = quantity of heat.
J = the ratio between the unit of heat and the unit of work.
K_v = the specific heat of a gas at constant volume in units of work.
K_p = the specific heat of a gas at constant pressure in units of work.
γ = ratio of the specific heats of gases.
k = conductivity.
L = latent heat.
m = mass.
μ = micron = ·001 mm.
P = pressure.
$R = \frac{PV}{\theta}$.
r = electrical resistance.
ρ = absolute density.
S = specific heat.
s = space.
t = time.
τ = temperature as read by the mercurial thermometer.
θ = absolute temperature or temperature by the air thermometer.
ϕ = entropy.
V = volume; V_o volume at 0° C.; V_τ volume at τ° C.
v = velocity.
W = work.
y = coefficient of expansion of liquids.
z = " " " solids.

FORMULÆ

$F. - 32 = \frac{9}{5}C. = \frac{9}{4}R.$ ....Scales of temperature, p. 12.

$l_\tau = l_0\,(1 + z\tau)$ ....Linear expansion, p. 18.

$V_\tau = V_0\,(1 + y_1\tau + y_2\tau^2)$ ....Expansion of liquids, p. 59.

$V_\tau = V_0\,(1 + a\tau)$ ....Expansion of gases, p. 49.

$y_\tau = \frac{1}{V_0} \cdot \frac{dV}{d\tau}$ ....True coefficient of expansion, p. 58.

$h_0 = h\frac{1 + z\tau}{1 + y\tau}$ ....Reduction of barometer reading, p. 38.

$\frac{V_1P_1}{\theta_1} = \frac{V_2P_2}{\theta_2}$ ....Gaseous laws, p. 53.

$S = \frac{H}{m(\tau_2 - \tau_1)}$ ....Specific heat, p. 67.

$-\frac{d\tau}{dt} = M(\tau_1 - \tau_2)$ ....Newton's Law of Cooling, p. 210.

$-\frac{d\theta}{dt} = M(\theta_1^4 - \theta_2^4)$ ....Stefan's Law of Cooling, p. 222.

$H = kA\frac{\tau_1 - \tau_2}{l}t$ ....Conductivity, p. 186.

$JH = C^2rt$ ....Joule's law, p. 175.

$r_\tau = r_0\,(1 + a\tau + b\tau^2)$ ....Variation of electrical resistance, p. 177.

$W = fs = \frac{1}{2}mv^2$ ....Kinetic energy, p. 279.

$W = JH$ ....First law of Thermodynamics, p. 290.

$W = PV \times 2{\cdot}3026 \times \log.\frac{V_1}{V_2}$ ...Work in isothermal expansion, p. 336.

PV^γ = a constant ....Adiabatic curve, p. 354.

$W = \frac{1}{\gamma - 1}\{P_1V_1 - P_2V_2\}$.......Work in adiabatic expansion, p. 355.

$\frac{W}{H} = \frac{\theta_2 - \theta_1}{\theta_2}$ ....Efficiency of perfect engine, p. 374.

$P = \frac{2}{3}E = \frac{1}{3}\rho v^2$ ....Energy of unit volume of gas, p. 314.

HEAT

AND THE PRINCIPLES OF THERMODYNAMICS

Part I.—Experimental

CHAPTER I

INTRODUCTORY

1. Everyone is familiar with the sensations of heat and cold. The physical cause of these sensations is what we mean by the term Heat. Taking the idea of heat which our sensations yield as sufficient for practical recognition of what is meant by the term, we proceed to note briefly a few facts of common experience that will serve to indicate the main outlines of a more extended view of the subject.

If we mix some hot and some cold water together, the resulting mass of water is cooler than the original hot, and hotter than the original cold water. Evidently heat has been transferred from one mass of water to the other. *Heat, then, is transferable.*

A rough experiment will soon establish the fact that if five minutes are occupied in melting a pound of ice over the flame of a Bunsen burner, it will take about ten minutes to melt two pounds of ice over the same flame. We may say that the heat transferred in the one case is double that transferred in the other. We can thus think of heat as capable of being measured, and therefore of numerical estimation; and when we can deal with it in quantities, the idea of heat has become more precise and scientific. *Heat is a measurable quantity. The process of measuring quantities of heat is called* **calorimetry.**

2. EFFECTS OF HEAT.—The effects which heat produces are very various; nearly every property of a body is affected by the addition or withdrawal of heat. The principal effects to be here treated of are (*a*) change of temperature, (*b*) change of volume, and (*c*) change of physical state.

In addition to these changes, addition or withdrawal of heat produces changes in the electrical condition of bodies generally, in the magnetic condition of magnetic substances, in the optical properties of transparent substances, and in chemical affinity and solvent power.

(i) **Change of Temperature.**—When on touching two substances with the hand we say that one feels hotter than the other, we are speaking of temperature. The scientific way of saying that a body is growing hotter or colder is that the body is rising or falling in temperature. When heat passes into a body, the substance commonly, although not always, becomes hotter, i.e. *rises in temperature;* and when heat passes out of a body it commonly becomes colder, i.e. *falls in temperature.*

But temperature must be carefully distinguished from heat. "Heat is the property of matter concerned in producing our well-known sensation, and temperature is a certain variable quality of matter varying according to its temporary condition in respect of heat."[1] Thus we speak of *degrees* of temperature but of *quantities* of heat. When an absolute scale of temperature has been made, temperature may be regarded as a quantity. Change of temperature is one of the effects of the communication of heat to or the withdrawal of heat from a body. Changes of temperature are among the commonest of phenomena, and we have a special mode of sensation for appreciating them. Temperature is measured by the thermometer, and that part of the Science of Heat which is concerned with the measurement of temperature is called **thermometry.**

Take two exactly similar vessels of thin iron, and place in one a pound of mercury and in the other a pound of water at the same temperature. If these two vessels be similarly exposed to the same source of heat for a short time, the temperature of the mercury will rise much higher than that of the water, although the quantities of heat absorbed in the two cases cannot have been very different. If the vessels be first heated to the same temperature and then placed in equal masses of cold water, the rise of temperature produced in the respective masses of water will not be the same.

[1] *Ency. Brit.* art. Heat.

Equal masses of mercury and water, therefore, do not take in or give out equal quantities of heat in undergoing equal changes of temperature. This is expressed by saying that the capacities for heat, or **thermal capacities**, of water and mercury are different. Each substance has a specific thermal capacity just as it has specific gravity.

(ii) **Change of Volume.**—If a small quantity of air be tied up in a bladder and placed near a fire, a large increase of size is at once apparent. If a flask exactly full of water be heated, some of the water will overflow. If a platinum wire be tightly stretched between two supports and then heated to white heat, its length will be visibly increased.

These and numerous facts of a similar nature establish the general rule, that *bodies expand when heated and contract when cooled.*

If a very hot liquid be poured into a glass vessel, the vessel is liable to be cracked, owing to the strains set up by the expansion of the inner portion while the outer surface is still cold. Glass touched with a piece of hot metal will crack.

The riveting together of boiler plates is generally done with red-hot rivets, which on cooling contract and pull the plates very close together. The same principle is taken advantage of in the building of heavy guns. These are formed of a number of concentric cylinders of steel which are successively slipped into position in a red-hot condition, the inner cylinder or cylinders being cold. The enormous pressure upon the innermost cylinder, which results from the contraction of the outer ones, enables it to withstand the pressure of the gases produced by the explosion of heavy charges of gunpowder. A similar process is adopted in fitting iron tires on wheels. Railway metals are laid with a small space between them to allow for contraction and expansion. Furnace-bars for like purpose are never tightly fixed, and gas-pipes are laid with telescopic joints.

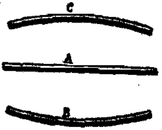


Fig. 1

The amount of expansion for any given rise of temperature is different for each substance. This may be illustrated by riveting together thin bars of different metals. Then, if these compound bars are straight at ordinary temperatures, they become curved when they are either heated or cooled. Thus, if in the bars shown in fig. 1 the unshaded portion represent silver and the shaded portion platinum, on a rise of tem-

perature the bar bends as in C; on a fall of temperature it assumes the form shown in B, since silver elongates or contracts twice as much as platinum for the same change of temperature.

(iii) **Change of Physical State.**—The physical states are the forms in which matter can exist, viz. *solid*, *liquid*, and *gaseous*.

The characteristic property of a solid is **rigidity**, *in virtue of* which a solid offers a permanent resistance to any mechanical force tending to change its shape.

A *fluid*, on the other hand, offers no permanent resistance to any mechanical force tending to change its shape; if pressure be applied to a fluid in one direction only, it will, unless otherwise constrained, flow out in some other direction. A fluid must, therefore, be contained in a vessel, and it takes the shape of the vessel or portion of the vessel that it occupies.

In this characteristic the two classes of fluids, viz. liquids and gases, resemble each other. They differ from each other in respect of compressibility or extensibility.

A gas is a fluid, the volume of which may be increased to any extent by reduction of the pressure to which it is subject. A gas completely fills any vessel in which it is placed, and possesses no free surface.

A *liquid* is a fluid, the volume of which does not continue to *increase indefinitely as the pressure upon it is reduced.* A liquid has a free surface.

It is a fact of common experience that some substances, e.g. water, can exist in more than one state, as a solid, a liquid, or a gas; and that under ordinary atmospheric pressure the state of the substance is determined by its temperature. The liquid is the intermediate stage; addition of sufficient heat converts a liquid into a gas; subtraction of sufficient heat converts a liquid into a solid.

Fusion or **melting** is the name given to the process of change that takes place when a solid becomes a liquid; its converse is **solidification**.

When a liquid passes into the gaseous state the process is called **vaporization**; and the converse process, when a substance passes from the gaseous to the liquid state, is **condensation**. Vaporization may take place in two ways, by **evaporation** and by **ebullition** or **boiling**.

Some solids, such as arsenic and camphor, readily pass from solid *to gas or from gas to solid without becoming liquid at all;* these are said to **sublime**, and either process is called **sublimation**.

Place a mass of pounded ice at freezing point in a vessel and pour a little hot water upon it. A thermometer immersed in the ice *indicates no rise of temperature; whereas, if the experiment* be repeated with a mass of water at freezing poiut, a rise of temperature results. And again, water under ordinary conditions boils at a certain temperature called boiling point, and cannot be made any hotter however high the temperature to which it may be exposed.

When heat is thus added to a substance, without rise of temperature, the heat is said to be rendered **latent.** Latent heat is heat that is absorbed by the substance during the change of state from solid to liquid, or from liquid to gas. It does not raise the temperature of the substance.

(iv) **Changes in other Properties.**—There are many other properties of matter which are modified by heat. Changes in the electrical condition of bodies that ensne on the addition or subtraction of *heat are treated of in Chapter XIII. The character of the radia*tions emitted from a hot body varies greatly with the temperature and produces very different results. Such properties as plasticity, viscosity, surface tension are also affected.

3. SOURCES OF HEAT.—The prime source of our heat is, of course, the sun. By his rays the general temperature of the surface of the earth and of the atmosphere is maintained. The heat reaching us directly from the sun is also made use of occasionally to accomplish definite objects, e.g. the extraction of salt from sea water.

The internal heat of the earth is also a direct sonrce which helps to determine the general thermal condition of the earth.

For special purposes, however, we draw upon secondary sources. Heat may be produced by chemical action, by change of physical state, and by currents of electricity. It is also produced in mechanical operations such as *friction, collision*, compression, torsion, &c., during change of the magnetic condition of magnetized bodies, and by spontaneous changes taking place in the structure of the atoms of certain bodies.

(i) **Chemical Action.**—The ordinary process of **combustion** of fuel is a chemical combination, most usually between carbon and oxygen or between oxygen and hydrogen. The heat of our bodies is maintained by exactly similar processes, which take place at a slower rate and thus produce only a moderate temperature.

(ii) **Change of Physical State.**—If steam be passed into water, the steam condenses and gives out large quantities of heat during

the change. This process takes place on a large scale in the atmosphere, and the heat given out during the condensation of the water vapour into rain has an important effect on climate. And similarly in solidification: if a mass of molten lead be placed in contact with ice, the lead solidifies, and in solidifying gives out heat which melts a quantity of the ice.

(iii) **Currents of Electricity.**—If an electrical current be passed through a wire, the wire becomes more or less heated. This is a convenient method of applying heat in particular cases.

(iv) **Friction.**—It is well known that a small piece of iron may be made red-hot by rapid blows with a hammer; a leaden bullet on striking a target is often melted; heat and sparks are produced when a railway train is stopped by a brake; and when timber is sawn or metal filed great heat is produced.

(v) **Radio-activity.**—The recent discovery of the radio-active substances indicates that there is probably a store of latent energy within the atoms of some kinds of matter which is gradually assuming the form of heat. The emission of heat from a gramme of radium amounts to as much as 100 calories per hour, and the process continues for many hundred years. Estimates of the amount of radio-active material present in the earth, and of the rate of its heat emission, indicate that the heat from this source may be an important factor in the maintenance of the heat of the earth and perhaps of the sun. The heat is supposed to be derived from the internal energy of the radium atom. This atom appears to consist of a system of smaller particles called electrons, and the expulsion of an electron from an atom at a high velocity produces the heat. Each atom acts as a source of energy.

4. MODES OF TRANSFERENCE OF HEAT.—Heat may be transferred from one body to another by **conduction**, by **convection**, and by **radiation**.

(i) **Conduction.**—If a short metal rod be held with one end in a flame, the other end becomes warm. The heat has passed from layer to layer of the rod, passing from the portion which is at a higher temperature to the portion which is at a lower temperature. This is the distinguishing feature of conduction.

(ii) **Convection.**—When hot water is admitted into one end of a bath and cold water into the other, there may be great difference of temperature between the ends of the bath. If the water be stirred the whole takes the same temperature. The heated water has travelled from one part to another carrying its heat with it.

This process is called convection. It is the principal mode by which heat is distributed through the mass of a fluid. Owing to the expansion that takes place on heating, the density of a fluid that is changing temperature is generally different in different parts. If the liquid be heated at the bottom, the force of gravity at once causes the upper, i.e. the denser portions, to fall and the less dense lower portions to rise, currents of fluid being thus set up which tend to equalize the temperature throughout. If a vessel of liquid be heated at the top these currents are not produced.

Winds are produced by the unequal heating of the air in different parts of the world by the sun's rays.

Hot-water or hot-air pipes are often used as channels by which a hot fluid may pass through and warm a building. The distinguishing feature of convection is that masses of a hot fluid serve as vehicles to convey the heat from place to place.

(iii) **Radiation.**—Heat often passes from one body to another without conduction or convection. If the hand be held in front of a fire the warmth is instantly felt, although a draught of air may be proceeding from the hand to the fire. And, moreover, heat passes with great facility through an ordinary vacuum and through some substances without warming them, conditions completely at variance with the processes of conduction and convection. This mode of transference is radiation. Its distinguishing features may be stated as the instantaneous character of the process, and the fact that the temperature of the medium may be unaffected by the passage.

5. NATURE OF HEAT—Since heat is transferable, it was formerly supposed to be a material but invisible fluid. The fluid was called **caloric**; its presence in larger or smaller quantities made bodies hot or cold. As a body weighs no more when hot than when cold, it was necessary that the fluid should be "imponderable". This hypothesis explained the transference of heat as the passage of a quantity of this fluid from one substance to the other; the expansion that results from heating was supposed to be due to the space occupied by the absorbed fluid; the change of physical state was akin to the process by which salt dissolves in water.

The caloric theory failed, however, to give any reasonable explanation of the production of heat by friction.

On the hypothesis that heat was a material fluid, where did the heat thus manifested come from? Two suggestions were made: first, that it came from surrounding bodies; and secondly, that the

thermal capacities of the two bodies rubbed together were diminished in the process, so that the quantity of caloric actually present was sufficient, under these conditions, to make the bodies hot. About 1795 Count Rumford, while engaged in boring cannon at Munich, turned his attention to the theory. His cannon became so hot that when surrounded by water they caused the water to boil. The caloric did not then come from the water surrounding the cannon, for this was hotter than before. Neither was the thermal capacity of the borings diminished by the disintegration they had undergone. The suggested explanation being thus inadequate, Rumford concluded that heat was not a material fluid, seeing that it could be produced to any amount, that the then received explanation of the heat produced by friction was not tenable, and that it was difficult to conceive anything to have been communicated to the mass of metal he operated upon except it were *motion*.

About the same time Sir H. Davy melted two pieces of ice by rubbing them together. It was known that the water produced had not a smaller but a greater thermal capacity than the ice, and the second of the suggestions mentioned above became untenable.

These experiments showed the caloric theory to be quite incapable of explaining the production of heat by friction. The hypothesis that the phenomena of heat are due to the motion of the molecules of which all substances are composed, has been since fairly established.

CHAPTER II

TEMPERATURE

The Thermometer

6. MEASUREMENT OF TEMPERATURE.—Within certain limits our sensations directly inform us as to the temperature of bodies we touch. A little attention, however, will show that our conclusion refers to the state of the external bodies only in their relations to ourselves. If the body touched abstract heat rapidly from or communicate heat rapidly to the hand, we have in the two cases respectively a sensation of great cold or one of great heat. Our sensation of temperature is connected with the passage of heat into or out of our bodies, and informs us of that fact of passage only.

Two bodies are at different temperatures when, on being placed in close communication, heat passes from one to the other. If under such conditions no passage of heat take place, the two bodies are at the same temperature, or in **thermal equilibrium.** We cannot always readily place two bodies in thermal communication with each other, but we can place each of them in turn in communication with a third body, and judge which is the hotter by their relative behaviour towards the third body. This is what is done when we use an ordinary thermometer.

Neither by our sensations nor by any other direct means are we able to measure temperature. But when heat is communicated to a body we have seen that not only does its temperature change, but other changes also take place simultaneously; and since we cannot measure the temperature itself, we are compelled to choose some particular substance, record some change that is easily capable of measurement, and assume that this change does really measure *the change of temperature. For ordinary purposes the substance* chosen is mercury confined within a glass vessel, the quantity that is directly measured being the apparent change of volume of the confined mercury. Then it is agreed to regard equal changes of volume as corresponding to equal changes of temperature.

7. THE MERCURIAL THERMOMETER.—The reason for choosing mercury is merely one of practical convenience. It is easily seen that if change of volume be taken as the variable, a fluid is better than a solid substance, because the mobility of a fluid enables us to determine where the change shall show itself. Thus we employ a large quantity contained in a reservoir, communicating with a slender tuhe, and nearly the whole change of volume manifests itself in the tube. If the bulb he large and the diameter of the bore very small, a small rise of temperature produces a considerable elongation of the mercury column.

Calibration of the Tube.—A glass tube is chosen, of which the bore is fine and as uniform as possible. It is, however, very improbable that the bore is of exactly the same size throughout its whole length, in which case equal increments of volume will not produce equal changes in the height of the column of mercury. For correct indications it is necessary that the volumes between two successive divisions marked on the stem should be equal. The tube is therefore **calibrated.** A small quantity of mercury is placed in the bore, and the length occupied by the mercury in successive portions of the tube is accurately measured. The length of a

division on the stem at any part is made proportional to the length occupied by this fixed volume of mercury. But for more accurate work it is necessary to form for each thermometer a table of corrections showing how much error is present at each point of its range. Such a table is often made for a finished thermometer by detaching from the thermometer column a short thread, and measuring its length in successive positions throughout the range of the instrument.

Introduction of the Mercury.—It is not possible to pour mercury directly into a fine tube. The following method of filling the tube is therefore adopted. A permanent closed reservoir, A (fig. 2), is blown at one end of the tube, and a temporary reservoir B is formed near the other. The interior having been made perfectly clean and dry,

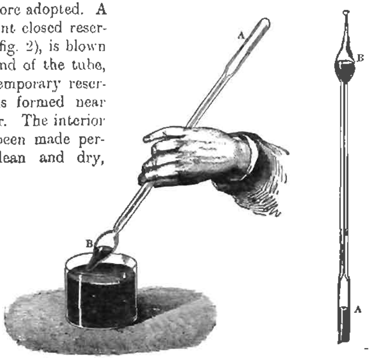


Fig. 2

its open end is placed under pure dry mercury which has been recently distilled, and the bulbs gently heated. Air is by this means driven out, and the bulbs being then allowed to cool, mercury is forced in by the pressure of the atmosphere. Of this mercury some passes into A, and some remains in B. When by alternate heatings and coolings the bulb A has become about half-full of mercury, it is customary to heat this mercury until it boils. The mercury vapour, as it passes out into the atmosphere, carries with it the remaining air, and when the last trace of the air has disappeared the closed reservoir and the tube are left completely

full of mercury. While still hot the instrument is sealed with the blowpipe at a point just below B, so that the stem is full of mercury at some temperature, just above the highest temperature to be measured.

After having been thus heated, the thermometer should be allowed to remain for a considerable period before the next operation.

Determination of the Fixed Points.—We now need two fixed points in order to form a scale of temperature. The two temperatures first suggested by Newton and generally adopted are those of melting ice, and of water boiling under standard pressure These temperatures are very constant and easily recoverable, and the temperatures required to be registered in the majority of our ordinary operations lie between them.

The thermometer is first placed with the bulb and the lower part of the stem in a vessel containing distilled water and small pieces of ice, and the position of the surface of the mercury marked on the tube. It is necessary that the ice and water should be pure, as impurities lower the melting-point of the ice.

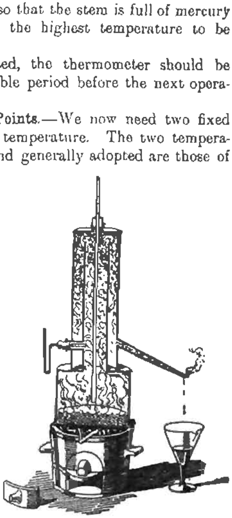


Fig. 3

The following method is described by Harker. He placed distilled water in a glass tube of about 300 c.c. capacity, and placed this in a vessel through which a strong solution of common salt at about -2° C. was constantly pumped. When the water was cooled to about $-\cdot5^\circ$ it was removed, and the thermometer being placed within it, a crystal of ice was also dropped in. The temperature quickly rose to freezing-point, and the thermometer indicated a steady temperature.

The instrument is then placed with its whole length in the steam of pure water boiling under normal atmospheric pressure in a vessel called a hypsometer, which is shown in fig. 3, and the position of the surface of the mercury is again marked. The tube in which the thermometer is placed is surrounded by a steam jacket in order to

check radiation from the thermometer, which would otherwise indicate too low a temperature. The height of the barometer is observed during this operation, and allowance made for deviation from the standard height. The reason for this is given in Art. 109.

The freezing-point is determined before the boiling-point (Art. 62), and the thermometer is immersed in the steam and not in the boiling water (Art. 112).

Graduation.—The length of tube between these two fixed points is then divided into smaller lengths called degrees, which mark equal increments of volume of the mercury within. If the bore be not uniform the length of these divisions will vary. The number of such divisions is a matter of arbitrary choice. Three scales are in use:—

Name.	Freezing-point marked.	Boiling-point marked.	No. of Divisions between Fixed Points.
Centigrade (C.) ..	0°	100°	100
Fahrenheit (F.) ...	32°	212°	180
Réaumur (R.)... ...	0°	80°	80

The Centigrade scale is almost universally employed in scientific work, and will be used throughout this book.

The division into degrees is continued above and below the fixed points. In any scale the readings below zero (0°) are marked minus, thus: $-16°$ R., which is the same as $-20°$ C. or $-4°$ F.

It is clear from the above table that 9 Fahrenheit, 5 Centigrade, and 4 Réaumur divisions occupy the same length on any given tube; **intervals of temperature** on the respective scales are therefore in the ratio of these numbers. If the zero on each scale were at freezing-point the numbers expressing the value of any particular temperature on the three scales would be in the inverse ratio of the lengths of the degrees, that is, if F, C, R be corresponding **temperature readings** on the F., C., and R. scales, we should have

$$F = \frac{9}{5}C = \frac{9}{4}R.$$

But since the Fahrenheit scale starts at 32° below freezing-point the relation becomes

$$\mathbf{F - 32° = \frac{9}{5}C = \frac{9}{4}R.}$$

This formula will serve to convert temperature readings from one scale to another.

Sensitiveness, i.e. the capacity to show small changes of temperature, depends on the relation between the volume of the bulb and the radius of the bore of the tube. If a be the internal radius of the bulb and l its length, then its volume (at 0° C.) $= \pi a^2 l$; and if a_1 be the radius of the bore and l_1 the length of the stem corresponding to a degree, then the volume of this part $= \pi a_1^2 l_1$. The increase in the volume of the mercury in the bulb when its temperature rises 1° C. is $\cdot 00018 \pi a^2 l$ (Art. 28),

$$\text{hence } a_1^2 l_1 = \cdot 00018 a^2 l.$$

By this formula any required degree of sensitiveness can be approximately calculated beforehand. Fig. 4 shows the upper and lower parts of a thermometer made to read to $\frac{1}{100}$ of a degree. In order that such thermometers may be of convenient length the range is limited to a few degrees, and both bulb and bore are large. They are used to record accurately temperatures which are very approximately known, or small variations in temperature. The reservoir at the top contains mercury some of which may, when required, be passed over into the stem, and thus vary the part of the temperature scale over which the thermometer can be used. The actual meaning of its indications in any case must be obtained by comparing its readings with those of a standard thermometer of long range.

Fig. 4

A fuller discussion of the mercury thermometer is given in Chap. XVII. One important practical point must be, however, noted thus early, viz. that the actual temperature recorded on any mercury thermometer is probably more or less incorrect for the following reason. When glass has been strained by force or strongly heated, some time elapses before it assumes a permanent state. During the filling of a thermometer it is of necessity strongly heated, and the bulb continues to contract for a long period after the process. If the zero point be determined before this gradual change is completed, as is often the case, the subsequent contraction of the bulb forces the mercury up the tube. Thus the starting-point or zero of the scale has been displaced, and all the readings are higher than they should be. This error may extend to as much as one division of the Centigrade scale. A temporary effect of this nature ensues when a thermometer, after having been immersed successively in melting ice and boiling water, is again placed in melting ice. The last temperature often reads ·2° or ·3° higher than the first. This temporary effect passes away in a week or two. The permanent error should be known and allowed for in every reading.

To make a practically perfect mercurial thermometer is a matter of great difficulty, and is not ordinarily a matter of necessity. All thermometers used in

important investigations are compared with a standard instrument, and a table of corrections is drawn up, by which the actual readings can be at once reduced to those of the standard instrument. This is done at the National Physical Laboratory for anyone who desires it.

8. THE ALCOHOL THERMOMETER.—Since mercury freezes at − 39° C., the mercury thermometer cannot be used to indicate very low temperatures. An alcohol thermometer may be used for this purpose. This instrument is based on exactly the same principles as the mercury thermometer. Absolute alcohol, a liquid whose freezing-point is below − 110° C., is often used. The graduation is partly performed by comparison with a mercury thermometer, and then continued downwards on the same scale. Alcohol expands much more than mercury when heated to the same extent. The degrees are therefore much longer than those of an exactly similar mercury thermometer, and the zero error of an alcohol thermometer is negligibly small. The instrument should he kept vertical when in use, because alcohol wets and adheres to the glass.

Since alcohol boils at 78° such thermometers may also be used to measure many ordinary temperatures. They possess the advantage of greater sensitiveness than the ordinary mercury thermometer owing to the larger coefficient of expansion; and since the specific heat and density of the liquid are both low, they do not alter the temperature of small masses in which they are immersed so much as do mercury thermometers. To avoid distillation of the liquid it is sometimes necessary to warm the stem as well as the bulb.

9. MAXIMUM AND MINIMUM THERMOMETERS.—These thermometers are used for registering the highest and lowest temperatures reached during any given period. As the temperatures are recorded by the instruments themselves, they are called self-registering thermometers. The registration is often effected by means of a small piece of some suitable solid which is contained in the thermometer tube, and whose movements are controlled by the liquid. Every liquid behaves as though its surface were in a state of tension, and exerting a contractile force. To pierce the surface of a liquid requires a certain force, and the resistance to motion offered by these small solids is not sufficient to effect this. They are thus pulled or pushed along in contact with this layer, whose position they therefore record.

The oldest form is Six's, an alcohol thermometer in which the column of alcohol is broken by a thread of mercury (fig. 5). It is both a maximum and a minimum thermometer. The large bulb C

is filled with alcohol and connected at the top with a U-tube into which the alcohol also extends, while the lower part of this tube is filled with mercury. A column of alcohol also fills the remainder of the U-tube, and may expand into the cup above. Immersed in the alcohol in each arm is a light steel index (shown enlarged at K). The instrument is "set" by bringing the indexes into contact with the ends of the mercurial column by means of a magnet, and as the alcohol in C expands and contracts, this column of heavy liquid moves one way or the other driving one of the indexes up the tube in front of it. The surface tension of the mercury is sufficiently great to prevent the index from entering the mercury, and a steel spring attached to its side presses against the glass and prevents the index from falling when the mercury retreats down either arm. In the figure the maximum temperature indicated is 60° and the minimum 18°.

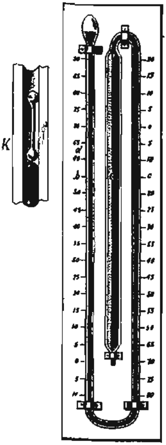


Fig. 5

Rutherford's Maximum and Minimum Thermometers are separate instruments. In the maximum thermometer the liquid is mercury, and the index (shown enlarged at *c* in fig. 6) is a small piece of steel or graphite.

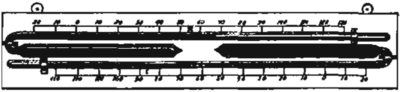
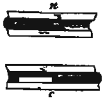


Fig. 6



This index is pushed in front of the mercury as the liquid column lengthens, and left behind when the mercurial column retreats.

In the minimum thermometer, which is widely used, the liquid is alcohol; the index (shown at *n* in fig. 6) is made of glass or enamel, and is placed

inside the liquid. When the alcohol expands it flows past the index, but when it contracts, the index is brought back just inside the retreating column. There is no spring attached to these indexes, *and the instruments must therefore be placed in a horizontal position.*

Negretti and Zambra's Maximum Thermometer is shown in fig. 7. Near the bulb at *a* the stem is contracted; when the mercury expands it forces its way past this obstruction, but on contraction none of the liquid returns into the bulb. The length

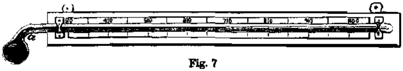


Fig. 7

of the mercurial column in the stem thus serves to indicate the temperature to which it has been exposed. The instrument is set by shaking some of the mercury in the column down into the bulb until the bulb is full.

A **clinical thermometer** is a maximum thermometer of this type combining also the characteristics of the instrument of fig. 4. It is used by medical men to take the temperature of their patients, and is therefore made sensitive and of the limited range which their observations require.

The above instruments are those most generally used for the measurement of temperature. In some cases it is desirable or necessary to employ other means. A description of these is given in Chap. XVII.

10. EXAMPLE.

If when the temperature is 0° C. a mercury thermometer reads ·5° C., and when at 100° C. it reads 100·8° C., and if the bore of the stem is perfectly cylindrical and the degree divisions of equal length, what is the temperature when the *thermometer reads 20° C.?*

The length of the stem between 0° and 100° which should correspond to 100° C. corresponds really to 100·8 − ·5 = 100·3° C.

Hence 20 divisions on the thermometer correspond to 100·3 ÷ 100 × 20 = 20·06 true degree divisions. But the zero mark 0° corresponds to a true temperature of ·5°, therefore the true temperature when the thermometer reads 20° C. is 20·06 + ·5 = 20·56° C.

QUESTIONS AND EXERCISES

1. What readings Centigrade correspond to 50° F.? −3° F.?
2. What readings Fahrenheit correspond to 10° C.? −39·4° C.?
3. The difference between two temperatures is 20 degrees Centigrade. Express that difference in F. and R. scales.

4. What temperature is expressed by the same number in the Fahrenheit and Réaumur scales?
5. What temperatures between 40° F. and 50° F. are expressed by whole numbers on the C. scale?
6. What temperature on the C. scale is expressed by a number three times as large as that expressing the same temperature on the F. scale?
7. What condition must be fulfilled in order that a Centigrade and a Fahrenheit thermometer having the same bore may have their scale divisions of equal length?
8. The melting-point of tin is 235° C. What is it on the Fahrenheit scale?
9. A thermometer is graduated so that it reads 15 in melting ice and 60 in normal steam. Convert into Centigrade degrees the readings 20 and 90 taken on that thermometer.
10. Describe the construction and action of maximum and minimum thermometers.
11. What is meant by a "degree" on a thermometer, say 14° C.? What is change of temperature?

CHAPTER III

EXPANSION OF SOLIDS

11. LINEAR AND CUBICAL EXPANSION.—Solids expand in all directions when heated; but since the direct measurement of volume is somewhat difficult, the volume of a solid is nearly always calculated from linear measurements, and experiments on the expansion of solids are usually made on bars. The increase of length is called **linear expansion**, that of volume **cubical expansion**. A method of directly determining cubical expansion is given in Art. 32.

The following investigations apply to isotropic solids which expand equally in all directions. For the behaviour of crystals see Art. 61.

12. MEAN COEFFICIENT OF EXPANSION.—The change of length undergone by bars when heated has been frequently measured, and to make the results universally applicable they are expressed in a particular way.

Thus, suppose it is found that the length of a certain bar of metal at 0° C. is 25 in., and at 85° C. is 25·0375 in. Then

For 85° rise of temp. 25 in. lengthen by ·0375 in.

$$\therefore \text{ „ } 1^\circ \text{ „ } 1 \text{ „ „ } \frac{\cdot 0375}{85 \times 25} \text{ in.} = \cdot 0000176,$$

i.e. the bar lengthens by ·0000178 of its own length at 0° C. on a rise of one degree in temperature.

This number ·0000178 is called the **mean coefficient of linear expansion** of the rod between the temperatures 0° and 85°.

The mean coefficient of linear expansion of a solid is thus the nth part of the whole increase of length that takes place when a bar of unit length at 0° C. is heated from 0° C. to n° C.

If a bar whose length at 0° is a elongates by an amount x when its temperature is raised n°, then the mean coefficient of expansion between 0° and n° is $\frac{1}{n} \cdot \frac{x}{a}$. Since x is generally very small compared with a it is in practice generally sufficient to take a as the length of the bar at the ordinary temperature of the air. It must be noticed that the assumption is here made that the bar elongates n times as much when its temperature is raised n degrees as it does when the temperature is raised one degree.

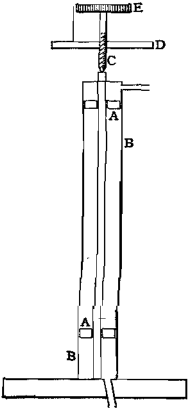


Fig. 8

We shall always employ the symbol z for the linear coefficient of a solid. Then if τ° be the temperature of any bar, we have

$$\frac{\text{Length at } 0^\circ}{\text{Length at } \tau^\circ} = \frac{l_0}{l_\tau} = \frac{1}{1 + \tau z}.$$

13. METHODS OF DETERMINING COEFFICIENTS. — To determine the coefficient of expansion of a metal bar it is necessary to know accurately the length of the bar at two different known temperatures. The smallness of the expansion constitutes the chief difficulty. Two methods may be employed: either the increase in length may be directly observed by means of a microscope, or obtained from the readings of a spherometer or of a wedge; or means may be used of multiplying the effect in a known ratio. On the former principle a method in common use, which takes somewhat different forms in different laboratories, may be understood by reference to fig. 8. The bar A is enclosed in a tube B through which

steam or other suitable vapour may be passed, and thus any desired temperature established. One end of the bar is fixed in position either by resting on a small slate slab or by clamping. To the other end is applied the extremity of a fine screw C which works through a plate D, and possesses a large head E having its circumference marked with a hundred divisions. A spherometer is suitable. The plate D being fixed in position, the bottom of the screw C is brought into contact with the free end of the bar at the higher and again at the lower of the two temperatures of the bar. The difference of length is obtained from the indications of the screw. The number of complete turns of the screw and the fraction of a turn, and also the pitch of the screw being known, the difference of length caused by the change of temperature of the bar is obtained. The whole length of the bar at the temperature of the laboratory must of course also be measured.

$$\text{Then since } l_\tau = l_0 (1 + z\tau),$$

$$\text{we have } \frac{l_{\tau_1}}{1 + z\tau_1} = \frac{l_{\tau_2}}{1 + z\tau_2},$$

and τ_1 τ_2 and l_{τ_1} l_{τ_2} (the lengths at the two temperatures) being known, z is calculated.

14. **Method of Laplace and Lavoisier.**—The apparatus employed by Laplace and Lavoisier, in which the expansion is magnified to a known extent, is indicated in fig. 9. The bar AB mounted on rollers was firmly fixed at one end A, while the other end B was in contact with a lever OB attached at right angles to the axis of a telescope, L, which was pivoted at O and directed towards a distant scale CC′.

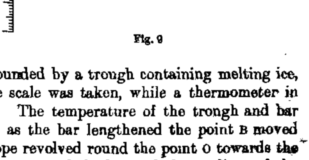


Fig. 9

The bar AB was first surrounded by a trough containing melting ice, and the reading C on the scale was taken, while a thermometer in the trough was also read. The temperature of the trough and bar was raised gradually, and as the bar lengthened the point B moved towards B′ and the telescope revolved round the point O towards the position L′OL′. The temperature of the bar and the readings of the

telescope scale were simultaneously taken as the process continued. The actual expansion BB′ corresponding to the scale reading CC′ was obtained from the ratio between the similar triangles OBB′ and OCC′.

Thus BB′ : CC′ :: OB : OC;

$$\text{whence } BB' = \frac{OB}{OC} CC'.$$

The telescope may be replaced by a mirror on to which is directed a ray of light that is reflected back on the scale. This arrangement doubles the deflection CC′, for the deviation of the ray of light is double that of the mirror.

15. **Method of Ramsden and Roy.**—One of the best methods is that of Roy and Ramsden, the chief portions of whose apparatus are shown in fig. 10. Three troughs, A′, B, A″, are placed parallel to

Fig. 10

each other on a horizontal slab; A′ and A″ each contain an iron bar, and B contains the bar to be experimented on. All the bars have one end firmly fixed. At a short distance from each end of each bar is fastened a vertical arm which rises above the top of the trough. The two uprights on the bar in A″ carry the eyepieces E, E′ of two telescopes; those on the bar inside B carry the object-glasses O, O′ of the telescopes; those on the bar inside A′ carry each a framework or plate PP′ on which is marked a fine cross. Each telescope is in two separate parts, but this is of no importance if the lenses are in the proper positions. Across the centre of the field of view in each of the tubes E, E′ is a fine vertical thread.

The three troughs are first filled with melting ice, and adjustments are made, so that on looking through E, E′ the vertical threads in E, E′ respectively appear to coincide with the vertical lines on P, P′. The trough B is then heated until the water in it boils, the bar within it expands, and, as the end at O is fixed, O′ is displaced towards the right in the figure. The upright carrying O′ also carries a micrometer screw, by means of which O′ is now carried back until

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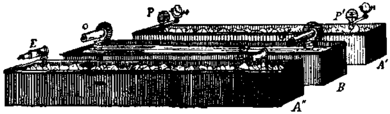

Fig. 10

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the vertical threads again appear to coincide as at first. No other part of the apparatus has moved, A′ and A″ being still full of melting ice. The indications of the micrometer screw show with great accuracy the distance through which O′ has moved. Thus the amount of expansion of the bar in B for a given rise of temperature is known, whence the coefficient is calculated.

16. The method of Ramsden, carried out with an elaborate refinement not before attempted, was employed by Benoît, who made many measurements of great accuracy. In this apparatus the microscopes were rigidly fixed to massive stone pillars, with their axes vertical and distant from each other by a length L, which was very accurately known. Each experimental bar had a fine mark near each end, the distance M between these two marks being very nearly the same as the distance between the axes of the microscopes. This bar, placed in a trough through which circulated water of a known temperature, was accurately adjusted in the plane of the reading microscopes, and the difference between L and M was measured by a micrometer scale. The distance between the marks on the bar at various temperatures was thus determined with great accuracy.

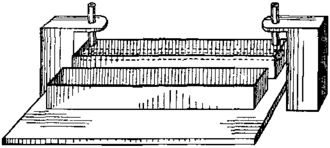

Fig. 11

The following application of this method is readily practicable. The measuring apparatus consists of an accurately graduated bar, along which slide two microscopes, having cross wires in the eyepieces, and micrometer screws by which the instruments may be moved along the graduated bar. The distance between the centres of the eyepieces can by this means be accurately determined.

The experimental bar has a fine cross scratched on it near each end, and being placed inside a suitable glass tube parallel to the graduated bar, the microscopes are adjusted until the centre of each cross is in the centre of the field of view when the temperature is that of the room. Thus the distance between these two points is known. Steam is then passed through the glass tube, and when the experimental bar has taken the temperature of the steam, the

microscopes are again adjusted so that the centres of the crosses are again in the centres of the fields. The sum of the distances through which the microscopes are moved gives the elongation of the bar. Care must be taken that the temperature of the measuring bar remains unchanged during the process.

It is not necessary for the microscopes to actually slide along such a bar; they may be clamped to a table or to a stone slab, and an ivory graduated scale be placed in position for the purpose of taking the distances between the centres of the eyepieces when in their original position, and the change may be read by a scale in the eyepiece.

17. **Expansion of Crystals.**—A method proposed by Fizeau has been employed for substances such as quartz, graphite, tourmaline, &c., which can only be obtained in short bars. The principle of the method may be understood by reference to fig. 12. The substance in the form of a plate A with polished plane faces is placed upon a metal disk B,

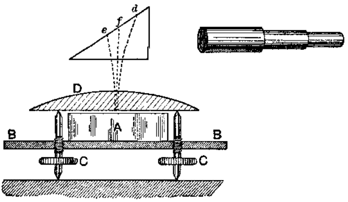

Fig. 12

through which pass supporting screws C, having a very fine thread. Upon the top of these screws rests a plano-convex lens D with the plane surface adjacent, parallel and very near to A. The point *f* is the focus of this lens, and on placing a small source of light at *d* and the eye at *e*, a system of concentric rings alternately dark and light is seen, produced by the interference of rays of light that have pursued slightly different paths on their way from *d* through D to A and back thence to *e*. Any change in the distance between D and A is shown by an enlargement or contraction of these rings. When this apparatus is subjected to change of temperature the screws C and the plate A expand upward, and the difference between these dilatations is the change in thickness of the air layer. The coefficient of expansion of the screws being known, that of the substance A is then calculable if the change in the thickness of the layer of air is known.

In Benoît's measurements the apparatus was enclosed in a chamber with double walls in which any desired temperature could be maintained. The light used proceeded from a lamp having a salted wick, and being directed horizontally on to the vertical face of a totally reflecting glass prism which was placed vertically over the lens and specimen, was reflected down to the surface of A. After reflection from this surface the light passed up again to the reflecting prism and was received into a telescope. As the light was monochromatic, the fringes were alternately dark and yellow. When the thickness of the air layer was diminished, these fringes crossed the centre line of the field of view of the telescope.

Let λ = the wave length of the light employed, and

n = the number of fringes that passed the centre of the field of vision while the temperature changed from τ_1 to τ_2;

then $n \times \frac{\lambda}{2}$ = the diminution in the thickness of the air space.

This is equal to the difference between the expansion of the substance and the elongation of the supporting screws, i.e.

$$(l_1 z_1 - l_2 z_2)(\tau_2 - \tau_1)$$

where l_1 = the thickness of the slice of crystal,
z_1 = its coefficient of expansion,
l_2 = the length of the supporting screws,
z_2 = their coefficient of expansion.

Hence $n \times \frac{\lambda}{2} = (l_1 z_1 - l_2 z_2)(\tau_2 - \tau_1)$.

The value of z_2 was found by removing the crystal and repeating the observation, using the polished base of the tripod as the reflecting surface. Measurements by this method have recently been made on metals at low temperatures.

Some results are given in the table in the Appendix.

18. METHODS OF COMPENSATION FOR EXPANSION.—The change of length that takes place with change of temperature is sometimes a serious difficulty. Two of the most important physical measurements are those of length and time. Change of temperature affects bars used to measure lengths, and the metallic parts of watches and clocks. Various devices are in use to remedy this inconvenient liability to variation.

19. **Standards of Length.**—Our British standard of length is defined with reference to the temperature 62° F. (16·6° C.), and is correct only at that temperature. In the Indian survey a bar was

employed of the form shown in fig. 13, a brass bar *ab* and an iron bar *cd* being joined near the ends by cross pieces *ea* and *nb*. The expansions of brass and iron are in the ratio of 5 to 3, and therefore the lengths *ec* and *nd* were made $\frac{3}{5}$ of *ea* and *nb*. When the lengths *cd* and *ab* increased or diminished with change of temperature the arms *ea* and *nb* ceased to be parallel, but the distance between the points *e n* remained constant.

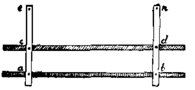

Fig. 13

A somewhat similar arrangement to the foregoing is adopted in the metal rods that connect the levers in railway signal-boxes with the points of the railway metals. In fig. 14, if A represent the end of a rod at the pointsman's lever, and D the other end at the points themselves, it is clear that if AD were a continuous rod the points at D might move with varying temperature without any movement of A. The rod is therefore arranged as shown, the part EF, which is cut out, being half the whole length. When the rods expand, A and D remain fixed, the result of the expansion being merely that the cross rods BE and CF rotate round the pivots HH.

Fig. 14

20. The Pendulum.—The theoretical or simple pendulum is a mass of matter collected at a point and suspended by a weightless string. In such a pendulum the time of vibration would be proportional to the square root of its length. The length of a real pendulum is the distance between two points called respectively the centre of suspension and the centre of oscillation. As this length is increased or diminished the pendulum vibrates slower or faster, and any clock governed by such a pendulum loses or gains. An ordinary seconds pendulum made of iron varies about six seconds a day for a change of temperature of 20° C. The following means are used to remedy this cause of error.

Harrison's Gridiron Pendulum consists of a framework of metal rods of the form shown in fig. 15, those marked F being generally of steel, and those marked C of brass. The arrangement is such that the steel bars are fixed at the top and in expanding lengthen downwards, while the brass bars are fixed at the bottom and in expanding lengthen upwards. The central steel bar passes freely through the lower cross bars and supports the bob. The remaining bars are in pairs, but for expansion purposes each pair may evidently be considered as constituting a single bar, so that there are practi-

cally three steel rods and two brass rods. Suppose their lengths at 0° are respectively s_1, s_2, s_3, b_1, b_2, and the coefficients of steel and brass respectively z_1 and z_2, then at τ° the bob has been lowered by an amount $(s_1 + s_2 + s_3)z_1\tau$, and raised by a length $(b_1 + b_2)z_2\tau$. In order that the effective length may have remained constant these changes must be equal.

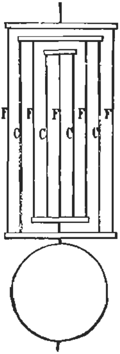

Fig. 15

$$\therefore (s_1 + s_2 + s_3)z_1\tau = (b_1 + b_2)z_2\tau.$$
$$\therefore \frac{s_1 + s_2 + s_3}{b_1 + b_2} = \frac{z_2}{z_1}.$$

i.e. the total lengths of the sets of rods must be to each other in the inverse ratio of their coefficients of expansion. This form of pendulum has been generally superseded by one based on the same principle, but made of zinc and iron, after the model of the great Westminster clock pendulum, the form of which is shown in fig. 16.

In this pendulum a central iron rod A carries a projection at the bottom on which rests a tube of zinc B. This zinc tube is surrounded by a larger iron tube C, the two tubes being joined at the top. The bob D is built round and connected to the iron tube. The coefficient of expansion of zinc is to that of iron in the ratio of 5 to 2, and hence the length of the zinc tube is two-fifths of the sum of the lengths of the iron rod and tube.

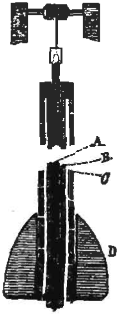

Fig. 16

In **Graham's Mercurial Pendulum** the bob consists of two glass cylinders containing mercury; the upward expansion of the mercury compensating the downward lengthening of the rod, and vice versa.

The best form of mercurial pendulum, however, is **Dent's**. In this pendulum the mercury is contained in a cast-iron cylinder, into the top of which the steel rod of the pendulum is screwed with its end dipping into the mercury. The metallic contact ensures the whole of the pendulum being at the same temperature.

21. **Balance Wheel of Chronometer.**—The indications of a chronometer depend upon the time of oscillation of the balance wheel. This period varies with the moment of inertia of the wheel, which depends upon the grouping of the mass of the wheel around its centre. In order that the period of oscillation of such a wheel should be constant, it is necessary that when the radii of the wheel lengthen the mass of the rim should move inward. The rim is made in three or more pieces, as shown in fig. 17, each piece being a compound bar with that *metal inside which has the smaller coefficient of expansion.* When the radius is lengthened the free end of the attached compound bar curves inward, and the mass of the rim is so adjusted by movable screws that the effects compensate each other.

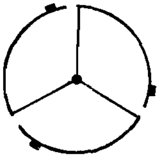

Fig. 17

22. LINEAR, SUPERFICIAL, AND CUBICAL EXPANSION.—Suppose we have a solid cube of copper whose edge is 1 cm. at 0°. Then at 100° the length of the edge is 1·0018 cm. The area of one face is therefore $(1{\cdot}0018)^2$, i.e. 1·00360324 sq. cm., and the volume $(1{\cdot}0018)^3 = 1{\cdot}005409725832$ c. cm. Now since it is not generally practicable to obtain the measurement of any length or volume correct to within $\frac{1}{100000}$ of the quantity to be measured, it is *practically useless* to retain any figures beyond the sixth. Omitting useless figures we have at 100°—

Length.	Area.	Volume.
1·0018 cm.	1·0036 sq. cm.	1·0054 c. cm.
i.e. 1 + (·0018) cm.	1 + 2(·0018) sq. cm.	1 + 3(·0018) c. cm.,

which shows that the coefficients of superficial and cubical expansion may be practically taken as respectively twice and three times the linear coefficient. The above may be made a general proof by replacing ·0018 by x, and neglecting all powers of x above the first.

It may be useful to point out that if a hollow vessel be heated the increase in volume of the interior is found by supposing that space to be filled with the same material as that of which the vessel is composed. For if we heat a hollow unit cube of metal whose walls are very thin, each edge elongating by an amount x, then the external volume of the cube becomes $(1+x)^3$ just as though it were solid. The increase in the thickness of the walls and the increase in the space they enclose are the same whether the interior be of metal or of air. The increase of

volume of the interior space is the increase of the solid cube that may or may not be there.

23. EXAMPLES.

1. If an iron bar be 2 ft. long at 0° C. and increase in length by a quarter of an inch when placed in a furnace, what is the temperature of the furnace? Coefficient of linear expansion = ·000012.

Let the temperature be x°.

$$\begin{aligned} \text{Then since } \tfrac{1}{4} \text{ in.} &= \cdot 0208 \text{ ft.,} \\ \text{length at } x^\circ &= 2\{1 + x(\cdot 000012)\} \\ &= 2\cdot 0208\,; \\ \therefore\ 2x \times \cdot 000012 &= \cdot 0208, \\ x &= 866\cdot\dot{6}^\circ \text{ C.} \end{aligned}$$

2. The coefficient of linear expansion of a certain metal is ·0000117. How much must the temperature of a block of the metal be raised in order that it may increase one per cent in volume?

Let x° C. be the rise in temperature,
then new vol. : old vol. : : $1 + x(\cdot 0000351) : 1$;
but new vol. : old vol. : : 101 : 100,

$$\begin{aligned} \therefore\ 100 + x(\cdot 00351) &= 101 \\ \therefore\ x &= \frac{1}{\cdot 00351} \\ &= 284\cdot 9. \end{aligned}$$

Ans. 284·9° C.

3. The linear coefficient of the expansion of iron being taken as ·0000123, find (in litres) the increase in the capacity of a cylindrical steam-engine boiler which at the freezing-point is 7 metres long and 3 in diameter when heated from 15° C. to 150° C.

$$\begin{aligned} \text{Coefficient of cubical expansion for } 1^\circ &= \cdot 0000369. \\ \text{Volume of boiler at } 0^\circ &= \pi(1\tfrac{1}{2})^2 \times 7 \text{ cubic metres.} \\ \text{,, \quad ,, \quad ,, } 15^\circ &= \tfrac{63}{4}\pi\{1 + 15[\cdot 0000369]\} \text{ c.m.} \\ \text{,, \quad ,, \quad ,, } 150^\circ &= \tfrac{63}{4}\pi\{1 + 150[\cdot 0000369]\} \text{ c.m.} \\ \therefore\ \text{Change of volume} &= \tfrac{63}{4}\pi\{135[\cdot 0000369]\} \text{ c.m.} \\ &= \tfrac{99}{2} \times 135 \times \cdot 0369 \text{ c.dm.} \\ &= 67\cdot 5 \times 3\cdot 6531 \text{ c.dm.} \\ &= 246\cdot 5 \text{ litres.} \end{aligned}$$

QUESTIONS AND EXERCISES

Linear coefficients of expansion required (per degree Centigrade).

Iron ... ·0000122.	Gold ... ·0000151.	Steel ... ·0000107.
Zinc ... ·000030.	Copper ... ·0000171.	Brass ... ·0000187.
	Glass ... ·0000084.	

1. **Describe carefully an accurate method of measuring the coefficients of expansion by heat of a solid, including the corrections and precautions that would probably be required in practice.**

2. Explain how to construct a seconds pendulum which shall keep correct time in hot and cold weather.
3. What change takes place in the diameter of an iron hoop which measures 80 cm. across at 10° C., when the temperature changes to 30° C.?
4. If the copper lightning-rod of St. Paul's be 500 ft. long at 40° F., find its length at 85° F.
5. A certain bridge is of iron, and 300 yd. long. Find its change in length during the year, assuming the range of temperature to be from −15° C. to 45° C.
6. A gridiron pendulum contains 3 ft. of iron rod. What length of zinc rod would be required to be used in its construction?
7. A glass bottle holds when quite full at the temperature of melting ice 20 c. in. of ice-cold water. How many cubic inches of boiling water will it hold, the bottle as well as the water being at 100 C.?
8. From London to York is 200 miles. Find the total space that must be left between the railway metals to allow for a temperature range of 100° F. if the rails are made of iron.
9. A bar of steel is 10 yd. long at 0° C. What will be its length at 30° C.?
10. If the steel rails of a railway are 8 yd. long, how far apart must they be placed to allow of a range of temperature of 35° F. above and below the temperature at which they were laid?
11. A bar of zinc measures 2·006 m. at 100° C. How long will it be at 0° C.?
12. The volume of a sovereign is ·02528 c. in. at 62° F. Find the change of volume of a million sovereigns in cooling from 62° F. to freezing-point, supposing them to be pure gold.
13. Find the change in area of a hollow copper ball 1 ft. in radius at 110° F. when exposed to a temperature of −20° F.
14. The end of an iron boiler is a circle 3 ft. in diameter at 0° C. What is the change in its area when heated to 100° C.?
15. A steel rod is measured with a brass scale. If the correct length of the rod at 0° is 74 cm., what would be the length at 15° as measured by the brass scale?

CHAPTER IV

EXPANSION OF LIQUIDS

24. The main phenomena of the expansion of liquids with increase of temperature may be shown by enclosing a number of suitable liquids in thermometer-shaped tubes (fig. 18) with large bulbs and heating them in a bath from the temperature of the air. The liquids should at the commencement all stand at the same height, *mn*, in the tubes. Then as the temperature is gradually raised these facts become apparent—

(i) The liquid in each tube rises considerably, showing a much

greater rate of expansion than solids exhibit. For example, mercury expands about seven times as much as glass.

(ii) The amount of expansion is different for each liquid. By making the experiment carefully with tubes of the same dimensions a fairly accurate practical idea of the relative apparent expansibilities may be obtained.

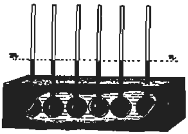

Fig. 18

25. ABSOLUTE AND APPARENT EXPANSION.—It is evident that in the previous experiment the containing vessels must also have expanded. The increase of volume observed in the liquids was the excess of the expansion of the liquids over that of the containing *vessels. This is called* **apparent expansion**. The **absolute expansion** of a liquid is the actual increase of its volume, which is equal to the sum of the increase of capacity of the containing vessel and the apparent increase of volume of the liquid.

If the absolute expansion of the liquid were equal to the increase of capacity of the vessel, the surface of the liquid in the tube would remain at the same level at all temperatures; and if the vessel expanded more than the liquid, the surface would sink in the tube as the temperature was raised.

This latter effect may be obtained by suddenly heating one of the bulbs by a flame, when the liquid sinks in the tube, because the bulb has expanded considerably before the liquid has begun to get warm. And conversely, if cold water be thrown on the bulb while it is hot, the rapid contraction of the solid forces the liquid up the tube.

26. Relation between Coefficients of Absolute and Apparent Expansion.—In dealing with liquids we are concerned with changes of volume only. The **mean coefficient of absolute expansion** of a liquid is the nth part of the whole increase of volume that takes place when unit volume of the liquid is heated from 0° to n°. We denote this coefficient by y. Suppose we have a quantity of liquid contained in a graduated tube, and let

V = real volume of liquid at 0° C.
y = coefficient of absolute expansion of the liquid for 1° C.

Then, omitting all consideration of the containing vessel, we have

$$\text{Volume at } \tau^\circ \text{ C.} = V(1+y\tau).$$

Now consider the expansion of the vessel whose coefficient (cubical) is z. Its capacity at τ° is greater than that at 0° in the ratio of $1 + z\tau$ to 1. The number expressing any fixed volume is diminished in the same ratio, and thus, as measured in such a vessel, a real volume V only appears as $\frac{V}{1 + z\tau}$, and therefore $V(1 + y\tau)$ appears as $\frac{V(1 + y\tau)}{1 + z\tau}$.

But if δ be the apparent coefficient of expansion of the liquid in glass, the apparent volume at τ° of that quantity of liquid whose volume at 0° was V is

$$V_\tau = V(1 + \delta\tau),$$

$$\therefore V(1 + \delta\tau) = V\frac{1 + y\tau}{1 + z\tau},$$

$$\therefore 1 + y\tau = (1 + \delta\tau)(1 + z\tau)$$
$$= 1 + (\delta + z)\tau + \delta z\tau^2.$$

If we neglect $\delta z\tau^2$ on account of its extreme smallness this reduces to

$$y = \delta + z.$$

The coefficient of absolute expansion of a liquid is thus very nearly equal to the sum of the coefficient of apparent expansion of the liquid and the coefficient of cubical expansion of the containing vessel.

27. *MEASUREMENT OF ABSOLUTE EXPANSION.*—There is one method by which the absolute expansion of a liquid may be directly determined. It is a fundamental hydrostatic principle that if a liquid be poured into a U-tube, it stands at the same height in both arms of the tube; but if two different liquids which do not mix be poured one into each arm, then the heights of the free surfaces above the level of the common surface are inversely proportional to the densities of the liquids.

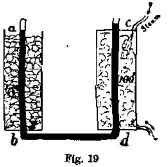

Fig. 19

Suppose then a U-tube *abdc* (fig. 19) to contain a quantity of liquid at 15° C.; the liquid will stand at precisely the same height in each arm. Now let the arm *ab* be surrounded with a cylinder containing melted ice, and the arm *cd* with a similar cylinder through which steam at 100° C. is kept circulating.

The liquid in *cd* expands and becomes less dense, while that in *ab* contracts and becomes more dense. A readjustment takes place until the column of less dense liquid balances the column of denser liquid. When a condition of equilibrium is established, if the height of the surfaces *a* and *c* above the axis *bd* of the connecting tube be measured, the length *ab* represents the volume of a quantity of liquid at 0°, and *cd* the volume of that same mass at 100°. This is quite independent of the expansion of the tube itself. If the tubes *ab* and *cd* be of different sectional areas the result is the same.

A rough experiment in which the difference of the heights of the columns is easily seen, may be made by substituting spirits of turpentine for mercury. It is best to choose the tube *bd* of smaller bore, in order to check currents in the liquid.

28. Expansion of Mercury.—As mercury is the substance generally used for thermometric purposes it is important that its coefficient of expansion should be accurately determined. Many measurements have therefore been made of this quantity. The first of any accuracy were made by Dulong and Petit. They surrounded the column *cd* (fig. 19) with a cylindrical bath of oil, heated by a furnace, and they determined its temperature by an air thermometer (Art. 193) immersed in the oil. The heights of the surfaces *a* and *c* were measured by a cathetometer (a telescope with its axis horizontal mounted on a vertical graduated metal bar). Their main results may be thus exhibited:—

Temperature.	0° C.	100° C.	200° C.	300° C.
Height of Column.	1	1·0180 = 1 + 100(·000180)	1·0368 = 1 + 200(·000184)	1·0566 = 1 + 300(·000188)

From these results it is clear that the coefficient for mercury is about ·00018, and the figures show that the expansion takes place at a gradually increasing rate as the temperature rises.

Several sources of error were present in these experiments, of which the most important were: (i) The coefficient of expansion assumed for air was Gay-Lussac's value, ·00375, whereas later researches show it to be ·00367. The temperatures recorded by the thermometer were therefore too low. (ii) The tops of the mercury columns when read were outside the baths, and the oil not being stirred was probably not at the same temperature throughout.

29. Regnault's Experiments.—Regnault in his repetition of

these experiments avoided these sources of error, and added to the sensitiveness of the apparatus by making his vertical tubes much longer (1·5 m.). His apparatus is shown in fig. 20.

Two vertical tubes of iron, AB *and* CD, *were connected near the* top by a horizontal branch AC, while at the bottom the arms BE and DF were connected by a bent tube EGF, from the top of which a tube GH led to a reservoir K containing air. *Mercury was poured* in at the top of A and C, and as it rose in the tubes EG, FG, air was pumped into K, so that *when the mercury just* filled the tube AC and overflowed from a small *hole on the upper side of* AC, it stood about three-fourths up each of the *tubes* EG, FG. *The surfaces* P and M were then at the same height above the axes of DE and *FD*.

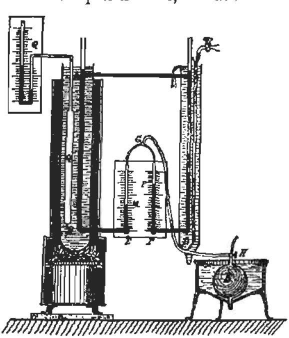

Fig 20

The column AB was surrounded throughout its whole height by a bath of oil of which the temperature was adjusted by a flame beneath. The temperature of the bath was maintained uniform throughout by a stirrer, and registered by an air thermometer Q (Art. 193).

The column CD was similarly surrounded by a bath of cold water kept in circulation by entering at the bottom and continually overflowing at the top, the temperature, which was maintained constant, being accurately ascertained by mercury thermometers placed at different depths. The tubes AC and BE were kept cool by water which overflowed upon them from the cold bath. When the oil-bath was heated and the temperature of the tube AB rose above that of CD, the mercury in AB dilated and some of it overflowed, the tube remaining full of mercury in a less dense condition. At the same time the surface of the mercury at M fell in the tube EM owing to the pressure of the air in K being greater than that exerted by the column of less dense mercury in AB.

30. Suppose the temperature of the warm bath to be raised to τ° C., and maintained steadily at that temperature, while that of all the rest of the apparatus is at 0° C., and let the height AB = CD = h_1, FP = h_2, and EM = h_3; then the pressure due to the mercury at M is that due to a column h_1 at temperature τ° C. *minus* that due to a column h_3 at temperature 0° C.; and the pressure at P is that due to a column $h_1 - h_2$ at 0° C. Now these are each equal to the pressure of the air in K. Therefore if y be the coefficient of expansion (or change of density) of mercury, reducing these heights to 0° C. we have

$$\frac{h_1}{1 + y\tau} - h_3 = h_1 - h_2$$

$$\text{whence } y = \frac{1}{\tau} \cdot \frac{h_2 - h_3}{h_1 - h_2 + h_3}.$$

In Regnault's experiments the cold column was not at 0° C., and the heights h_3 and $h_1 - h_2$ also required reduction.

31. The law of the expansion of mercury was deduced by means of a curve (see Art. 64). The numerical results are given in the table on page 246. These investigations of Regnault are of great importance, and the results are regarded as very accurate. They have, therefore, often been made the basis of further determinations.

32. Areometric Method.—This method consists in weighing a solid in the given liquid. It has been employed by Hällström and Matthiessen in investigating the expansion of water. It is necessary that the volume of the solid at the different temperatures should be accurately known, and to make the method sensitive the solid should be one whose rate of expansion is small compared with that of the liquid. Hällström determined the linear expansion of a rod of glass by Ramsden's method, and then formed the glass into a hollow sphere whose volume at any temperature could thus be accurately calculated. A quantity of sand was placed in the sphere sufficient to make it sink in water, and the sphere was then weighed in water at different temperatures. As the temperature of the water was raised, the volume of the sphere increased and the density of the water decreased. The volume of the water displaced (i.e. the volume of the sphere) being known for every temperature, and its mass being given by the indications of the balance, the density (mass/volume) was calculated for each temperature.

Matthiessen used pieces of glass cut from rods whose linear expansion he had previously determined.

The arrangement of his apparatus is indicated in fig. 21. The glass, suspended by a fine wire from one pan of a delicate balance dipped into distilled water, contained in a silver cylinder A, that stood in water contained in a vessel of zinc B.

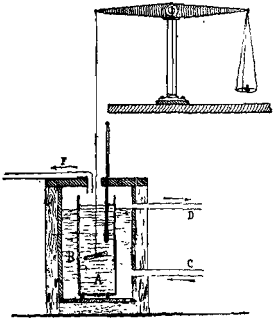

Fig. 21

The water in B was heated by means of a current of steam that entered at C, an overflow pipe D being provided to keep the water in B at a constant level. The existence of steam above the surface of the liquid was prevented by a draught pipe F. The zinc vessel was surrounded by a vessel of wood. The water in A was kept stirred, and its temperature indicated by a delicate thermometer. As the water grew hotter the apparent weight of the glass grew greater, and weights were added to the other pan of the balance. An example will illustrate the principle of the calculations and the order of the magnitudes observed. Thus suppose the following to be the data of an experiment:—

Temp.	Known Volume of Glass.	Weight in Air.	Weight in Water.	Mass of Water displaced.	Volume of Water displaced.
4°	1 c.cm.	2·75 grm.	1·75 grm.	1 grm.	1 c.cm.
100°	1·0025 c.cm.	2·75 grm.	1·79 grm.	·96 grm.	1·0025 c.cm.

Then density of water at 100°

$$= \frac{\text{mass}}{\text{volume}} = \frac{\cdot 96}{1\cdot 0025} = \cdot 9575$$

$$\therefore \frac{\text{Vol. at } 100^\circ}{\text{Vol. at } 4^\circ} = \frac{1}{\cdot 9575} = \frac{1\cdot 044}{1\cdot 000}.$$

And the mean coefficient of expansion of water between 4° C. and 100° C. comes out ·00044.

33. COEFFICIENTS OF APPARENT EXPANSION.—For

the determination of the coefficients of apparent expansion of liquids, two closely allied methods have been employed.

(i) **Kopp and Pierre**, whose experiments are among the best on this subject, enclosed their liquids in thermometers having large bulbs, and deduced the rate of expansion from the rise of the liquid in the stem. In this method it is necessary to know exactly the capacity both of the bulb and of the divisions on the stem.

Their apparatus is shown in fig. 22.

The given liquid contained in a thermometer A was placed vertically by the side of a similar mercury thermometer M in a bath B, which was heated by a furnace, and whose temperature was recorded by M. The stems of these thermometers passed through a smaller bath C, containing cold water, which entered by a pipe D and, leaving at E, maintained the stems at a constant temperature. Delicate thermometers m and a, containing mercury and the given liquid respectively, were placed in the upper cylinder, and served to indicate the corrections necessitated by this arrangement. (See Art. 37.)

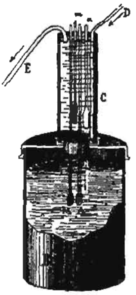

Fig. 22

The results obtained showed that the coefficients of expansion of all the liquids tried are of the same order of magnitude, ranging from ·00085 for bromide of phosphorus to ·0015 for ether; and that all liquids expand faster at high than at low temperatures.

By determining the expansion of mercury in their thermometers and using Regnault's result for the absolute expansion of mercury, Kopp and Pierre obtained the coefficient of expansion of the glass of which their thermometers were composed. This being known their observations of the apparent expansion of liquids served to give the absolute expansion.

This method is often adopted. Thus, suppose we wished to obtain the coefficient y for liquid alcohol we might proceed thus:—

(*a*) Observe the apparent expansion of mercury in some selected vessel. The absolute expansion of mercury being known, we can, as indicated in Art. 26, find the value of z for the vessel selected.

(*b*) Observe the apparent expansion δ of the alcohol in this same vessel for which z is known. And then the coefficient required $= \delta + z$.

An instrument in ordinary laboratory use for this purpose is the dilatometer or pyknometer, a form of which is shown in fig. 23. A

bulb A is connected at the top with a long graduated open tube B and at the bottom with a U-tube C of fine bore, which can be firmly closed by a padded stopper D.

The weight of mercury is found that at 0° C. fills the instrument from D to the zero of the scale on B; and also the weight that fills the whole tube up to some convenient scale mark on B. These observations give the volume of the bulb A and tube C together, and the volume of any measured length on the scale B.

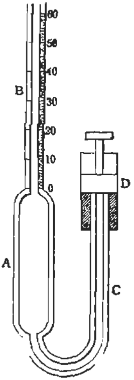

Fig. 23

Taking as known the absolute coefficient of expansion of mercury, observations taken at 0° C. and 100° C. with mercury enable the coefficient of dilatation of the vessel within those limits to be found. When this is known the coefficient of dilatation of any other liquid may be found by observing the rise of the liquid in the stem B for some definite rise of temperature.

(ii) **Weight Thermometer Method.**—Instead of observing the change of volume as indicated by the advance up a stem, we can cut the stem off at a certain point, keep the point immersed in mercury, and measure how much mercury flows in or out of the instrument when the temperature changes. Such an instrument is called a **weight thermometer**, and affords a convenient laboratory method of determining the relative expansions of a solid and a liquid, or of two liquids. The instrument is usually bent into the form shown in fig. 24. The vessel is first weighed when empty, clean, and dry. It is then filled with the liquid chosen by the method indicated in Art. 7. While cooling, its mouth must be kept under the surface of the liquid in order that the thermometer may be always quite full. The bulb is then placed for some time in melting ice or in a vessel of water of known temperature, and its weight when full at this temperature is observed. Subtracting the weight of the vessel, we thus know the mass of the liquid within the thermometer at the lower temperature chosen. The thermometer is then raised to a

Fig. 24 — Weight Thermometer

higher temperature in a bath. As its temperature rises some of the liquid overflows, and this is caught in a capsule and weighed. Subtracting this weight from that last obtained, we ascertain the mass of the liquid which fills the thermometer at the higher temperature.

Then if m_1 be the mass of the liquid that fills the thermometer when cold, and m_2 the mass that fills it when hot,

$$\frac{\text{Vol. at } \tau_2^\circ}{\text{Vol. at } \tau_1^\circ} = \frac{m_1}{m_2} = \frac{1 + \delta\tau_2}{1 + \delta\tau_1};$$

$$\text{whence } \delta = \frac{m_1 - m_2}{m_2\tau_2 - m_1\tau_1}.$$

Thus, suppose the liquid to be glycerine, and suppose

the weight of the empty thermometer	= 4·72	grm.
" " " thermometer full at 0°	= 14·14	"
" " " " " 100°	= 13·65	"
then the weight of the glycerine at 0°	= 9·42	"
and " " " " 100°	= 8·93	"

We thus have $\frac{9{\cdot}42}{8{\cdot}93} = \frac{1 + 100\delta}{1}$

$$\therefore\ \delta = \frac{1}{100} \cdot \frac{49}{893} = {\cdot}00054.$$

34. Dulong and Petit employed the weight thermometer to determine the coefficients of iron and platinum in the following

Fig. 25.—Expansion of Iron and Platinum

manner. A rod of the metal was placed in a glass tube (fig. 25), which was then drawn out at one end and filled with mercury at some known low temperature. On heating the apparatus the mercury that overflowed was a measure of the expansion of the solid *plus* that of the mercury *minus* that of the glass, and the two last being known the first was obtainable.

Let V_1 be the internal capacity of the vessel at 0°,
and V_2 the volume of the liquid at 0°,
and V_3 " " " solid " 0°;
then $V_1 = V_2 + V_3$.

Now let the apparatus be heated to τ°, then these volumes become

$$\begin{array}{lll} \text{for the vessel} & V_1(1 + z_1\tau), \\ \quad ,, \quad \text{mercury} & V_2(1 + y\tau), \\ \quad ,, \quad \text{solid} & V_3(1 + z_2\tau); \end{array}$$

and if V_0 be the volume at 0° of the mercury that escapes,

$$V_0(1 + y\tau) = V_2(1 + y\tau) + V_3(1 + z_2\tau) - V_1(1 + z_1\tau).$$

The volumes V_0 and V_3 may be determined by dividing the masses of the mercury and metal by their respective densities, and V_1 similarly from the weight of the mercury that exactly fills the vessel at 0°; V_2 is thus known. The coefficients y and z_1 being also known, the equation gives the value of z_2.

35. It is clear that the weight thermometer may, when the coefficients of expansion are known, be in turn used to indicate temperature; and for some purposes it is a preferable form of the mercury thermometer. It has the advantage that mass is capable of very exact determination, whereas the calibration of a stem is not a very exact operation. On the other hand, the instrument must be of considerable mass, and therefore absorbs a large quantity of heat, and thus under some circumstances may sensibly lower the temperature it is used to measure.

36. REDUCTION OF A BAROMETER READING.—This affords a useful example, and is often necessary in a laboratory, unless a set of tables accompany the barometer. Since the density of mercury changes with the temperature, a column of mercury, say 30 in. high, on a hot day, does not represent the same pressure as a column of the same height on a cold day. Hence it is necessary to reduce all barometer readings to some standard temperature, usually 0° C.

Suppose the temperature to be τ_0 C., then if y be the coefficient of expansion of mercury, the reduced height h_0 is less than the actual height h in the ratio of 1 to $1 + y\tau$. The observed height should therefore be divided by $1 + y\tau$.

If the height be measured by means of a metallic scale, a further correction is necessary on account of the change of length of the scale. Supposing this to be correct at 0° C., the effect of rise of temperature is evidently to make the divisions on the scale too long; and therefore the number of divisions occupied by the column of mercury is less than it should be in the ratio of 1 to $1 + s\tau$ where s

is the coefficient of linear expansion of the material of which the scale is made. The observed height h must thus be multiplied by $1 + z\tau$. Finally, the reduced height

$$h_0 = h \frac{1 + z\tau}{1 + y\tau};$$

or, what is very nearly the same, $h_0 = h\{1 + (z - y)\tau\}$. The value of z for brass is ·00001878 and y is ·00018018, whence

$$h_0 = h\{1 - \cdot 0001614\, \tau\},$$

when the scale is made of brass, and is correct at 0° C.

37. CORRECTION OF A THERMOMETER.—When, as is often the case, the stem of a thermometer is at a temperature considerably lower than that of the bulb, it is necessary to correct for the error thus introduced. Let the reading be τ_1 and the corrected temperature τ_0, when n divisions of the stem are at τ_2, the mean coefficient of apparent expansion of the liquid being δ.

Then a mercury column whose length is n divisions at τ_2 has to be corrected to the temperature τ_0. If this column were to rise in temperature from τ_2 to τ_0, the increase of height (which measures the increase of volume) would be $n\,\delta\,(\tau_0 - \tau_2)$ divisions. This, therefore, is the quantity to be added to the reading τ_1.

$$\therefore \quad \tau_0 = \tau_1 + n\,\delta\,(\tau_0 - \tau_2),$$

$$\text{or } \tau_0 = \frac{\tau_1 - n\,\delta\tau_2}{1 - n\,\delta}.$$

38. EXAMPLES.

1. A barometer having a brass scale correct at 62° F. reads 29·5 in. at 45° F. What is the pressure in true inches of mercury reduced to 32° F.?

Coefficient of linear expansion of brass for 1° F. = ·00001.
" " cubical " " mercury " = ·0001.

(i) *Scale Error.*—The scale divisions are too short because the scale is below its standard temperature. The reading is therefore too high in the ratio of $\{1 + 17(\cdot 00001)\}$ to 1.

The corrected reading is $29{\cdot}5 \div 1{\cdot}00017 = 29{\cdot}49598$ in.

(ii) *Error in the Mercury Column.*—Since the reading is 45° instead of 32° the corrected height will be less than the actual height in the ratio of $1 - 13(\cdot 0001)$ to 1.

$$\therefore \text{ True height } = 29{\cdot}49598\{1 - 13(\cdot 0001)\}$$
$$= 29{\cdot}457.$$

2. A glass bulb with a uniform fine stem weighs 10 grm. when empty, 117·8 grm. when the bulb only is full of mercury, and 119·7 grm. when a length

of 10·4 cm. of the stem is also full of mercury. Calculate the relative coefficient of expansion for temperature of a liquid, which, when placed in the same bulb, expands through the length from 10·4 to 12·9 of the stem when warmed from 0° C. to 28° C. The density of mercury is 13·6 grm. per sq. cm.

The mercury that fills the bulb weighs 107·3 grm.,

$$\therefore \text{ the volume of the bulb is } \frac{107\cdot3}{13\cdot6} = 7\cdot89 \text{ c.cm.}$$

Similarly, the volume of 1 cm. length of the stem is

$$\frac{119\cdot7 - 117\cdot3}{10\cdot4 \times 13\cdot6} = \frac{2\cdot4}{10\cdot4 \times 13\cdot6} = \cdot017 \text{ c.cm.}$$

Of the liquid the original volume is

$$7\cdot89 + 10\cdot4\,(\cdot017) = 8\cdot069 \text{ c.cm.}$$

And the increase of volume is

$$2\cdot5\,(\cdot017) = \cdot0425\,;$$

$$\therefore \text{ the coefficient of expansion } \delta = \frac{\cdot0425}{8\cdot069} \times \frac{1}{28} = \cdot000188.$$

3. The weight of mercury which completely fills a specific-gravity bottle at 0° C. is 15 oz.; when the temperature is raised to 100° C. the contents weigh 14·77 oz. If a piece of copper is put into the bottle, and the latter filled with mercury, the weight of the contents at 0° C. is 13·3 oz., and at 100° C. is 13·12 oz. Find the coefficient of expansion of the copper, having given

Sp. gr. of mercury at 0° C. = 13·6.
„ copper „ = 8·6.
Coefficient of expansion of mercury = ·00018.

(1) To find the volumes of the substances at 0° C.

$$\text{Since volume} = \frac{\text{mass}}{\text{density}},$$

$$\therefore \text{ Capacity of bulb in arbitrary units} = \frac{15}{13\cdot6} = 1\cdot103.$$

Now suppose the volume of the copper placed in the mercury to be x such units, then its mass = $8\cdot6x$ units; and that of the mercury displaced = $13\cdot6x$ units. Thus the loss of weight is $13\cdot6x - 8\cdot6x$ units.

$$\therefore (13\cdot6 - 8\cdot6)x = 15 - 13\cdot3\,;$$
$$\therefore x = \cdot34.$$

The volume of the copper is thus ·34 unit, and that of the mercury is 1·103 − ·34 = ·763 unit.

(2) Coefficients of mercury and glass.

$$\text{The apparent coefficient of mercury in glass} = \frac{15\cdot00 - 14\cdot77}{14\cdot77}\cdot\frac{1}{100} = \cdot000156\,;$$

$$\text{and the real coefficient} = \cdot00018\,;$$

$$\therefore \text{Coefficient of glass} = \cdot000024.$$

(3) Then with the notation of Art. 33 we have

$$\begin{aligned} V_1 &= 1{\cdot}103. & \qquad & & y &= {\cdot}00018. \\ V_2 &= {\cdot}763. & & \text{and} & z_1 &= {\cdot}000024. \\ V_3 &= {\cdot}34. & & & z_2 &\text{ is to be found.} \end{aligned}$$

$$\text{Also } V_0 = \frac{13{\cdot}3 - 13{\cdot}12}{13{\cdot}6} = {\cdot}0132.$$

$$\begin{aligned} \therefore\ {\cdot}0132\,(1 + {\cdot}018) &= {\cdot}34\,(1 + 100z_2) + {\cdot}763\,(1{\cdot}018) - 1{\cdot}103\,(1{\cdot}0024); \\ \therefore\ {\cdot}34 + 34z_2 &= 1{\cdot}103\,(1{\cdot}0024) - 1{\cdot}018\,({\cdot}7498), \\ 34z_2 &= 1{\cdot}10565 - {\cdot}7633 - {\cdot}34 \\ &= {\cdot}00235; \\ \therefore\ z_2 &= {\cdot}000069. \end{aligned}$$

QUESTIONS AND EXERCISES

[When not stated, the coefficient of absolute expansion of mercury may be taken as ·000181. For other substances see the tables.]

1. Distinguish between the coefficient of apparent expansion and the coefficient of absolute expansion of a liquid. Describe Regnault's method of determining the coefficient of absolute expansion of mercury.
2. Describe the ordinary process of determining the coefficient of expansion of a liquid like alcohol or paraffin, remembering the necessary preliminary determination of the expansibility of the glass vessel employed.
3. What would be the effect of heat on a thermometer if the coefficient of expansion of the liquid were ·0001 and that of the envelope ·0002?
4. Given the absolute coefficient of expansion of mercury and the cubical coefficient of expansion of glass, show how to find the apparent coefficient of expansion of mercury in glass.
5. How may the absolute expansion of any non-volatile liquid be directly determined? Explain why the balancing of a hot against a cold column eliminates the expansion of the vessel. If the cold column at 4° C. were 60 cm. high, and the hot column at 95° C. were $\frac{1}{3}$ cm. higher, what would be the absolute coefficient of cubical expansion of the liquid?
6. A glass bottle holds, when quite full, at the temperature of melting ice, 20 c. in. How many ounces of boiling water will it hold?
7. If the coefficient of apparent expansion of mercury in glass be $\frac{1}{6500}$, what mass of mercury will overflow from a weight thermometer which contains 400 grm. of mercury at 0° C. when the temperature is raised to 90° C.?
8. Mercury is placed in a graduated straight glass tube, and occupies 100 divisions of the tube. Through how many degrees must the temperature be raised to cause the mercury to occupy 101 divisions?
9. Find the reading of a thermometer whose bulb is at 100° C. while the stem is at 10° C., supposing that the zero is at the bottom of the stem.
10. A weight thermometer contains 176·7 grm. of mercury at 15° C., and only 174·4 at 100° C. Calculate the apparent expansion of mercury.
11. The liquid used in a certain thermometer has coefficient = ·001575; what difference would there be between this thermometer and the mercury thermometer?
12. A barometer with a brass scale which has been adjusted at 0° C. stands at

778 mm. when the temperature is 20° C. What pressure in kilograms per square cm. does this *indicate?*

13. A solid at 0° C. when immersed in water displaces 500 c. in.; at 30° C. it displaces 503 c. in. Find its mean coefficient of linear expansion between 0° and 30° C.

CHAPTER V

EXPANSION OF GASES

39. RELATIONS OF PRESSURE, TEMPERATURE, AND VOLUME.—In considering the expansion of solids and fluids no account was taken of the pressure to which the substances were subjected. *Under ordinary circumstances solids, liquids, and gases are alike subject to the pressure of the atmosphere.* The magnitude of this pressure is continually changing; but while such changes produce no appreciable effect on the volumes of solids or liquids, they produce a considerable effect on the volume which any given mass of gas will occupy. The resistance that air at atmospheric pressure offers to compression is only about one twenty-thousandth part of that offered by water. Hence the experimental study of the expansive effect of heat on gases is complicated by the effect produced by changes of pressure. These must therefore be considered.

The pressure of a gas is usually expressed in pounds per square inch or in grammes per square centimetre; or since, as in the case of the atmosphere, the pressure may be measured by the height of the column of mercury it supports, the pressure is often expressed in inches or centimetres of mercury. The pressure of the atmosphere is often called simply "an atmosphere".

Any portion of gas that is to be experimented upon must necessarily be confined in a closed chamber, on the walls of which it exercises a definite pressure. If one of those walls be movable, as is the case when air is confined by mercury in a tube, and if the pressure *on one face of the mercury be greater than that on the other,* movement ensues until the pressure on both sides is the same. The pressure *on* a gas is thus the same as the pressure *of* a gas, and we think often not of the pressure to which the gas is subjected, but of the pressure which the gas itself is exerting.

To describe the condition of a mass of gas we must state its volume, pressure, and temperature.

The statements of the relations between these three variables are the "gaseous laws".

We have to consider:—

(i) The relation between the volume V and the pressure P when the temperature τ remains constant.

(ii) The relation between the volume V and the temperature τ when the pressure P remains constant.

(iii) The relation between the pressure P and the temperature τ when the volume V remains constant.

40. RELATION BETWEEN P AND V WHEN τ IS CONSTANT. THE LAW OF BOYLE OR MARIOTTE.—By pouring mercury into a U-tube (fig. 26) closed at *a* and open at *b*, Boyle and Mariotte each found that the volume of the air in the arm *ac* was *inversely proportional to the pressure to which it was subjected.* If *cd* represent the common surface level of the mercury at starting, then in order to reduce the volume of the enclosed air to one-half of its original volume, i.e. to force the mercury up to the point *e*, the column of mercury *gh* must be of the same height as the barometer.

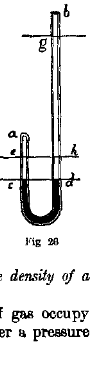

Fig 26

If more mercury be poured in at *b* until the enclosed air is reduced to one-third of the original volume, then the difference between the levels of the mercury surfaces is equal to twice the height of the barometer, the total pressure being three atmospheres. And so on. Boyle's law may be thus stated: *The volume of a quantity of gas varies inversely as the pressure;* or, since the density of a given mass varies inversely as its volume, the law may be stated: *The density of a gas is proportional to its pressure.*

Hence if at constant temperature a given mass of gas occupy a volume V_1 under a pressure P_1 and a volume V_2 under a pressure P_2 we have

$$V_1 P_1 = V_2 P_2 = \text{a constant.}$$

41. The tube of fig. 26 takes a more convenient form if the straight portions *a* and *b* are connected by a flexible indiarubber tube. Greater or less pressure on the confined air is then obtained by raising or lowering the arm *b*. The difference of level between the mercury surfaces is read on a scale placed behind the tube. In the apparatus shown in fig. 27 the U-tube has a flask F screwed on to one arm at the point *s*, and the larger volume of air thus dealt with makes the arrangement more sensitive than the simple Boyle's

tube. A graduated scale is placed beside each arm of the tube. A tap *m* serves to open and close communication between the arms as desired, and a tap *e* allows mercury to be drawn off when necessary.

The volume of the flask F, as well as that of the tube connecting F with *a*, is accurately known in terms of the divisions marked on the arms of the U-tube.

To prove the law for pressures lower than that of the atmosphere, mercury is poured into the tube at *b* until the surface level stands at *aa'*; the flask F, which is full of dry air, is then screwed on tightly, and some mercury is allowed to flow out by turning the tap *e*. The mercury will fall in both tubes, but not so far in *ac* as in *a'c'*. The difference between the two readings gives the amount by which the pressure of the air in F is less than that of the atmosphere in terms of the divisions on the scale, in terms of which also the height of the barometer is known. Several readings are thus taken. As the gas in F is allowed to expand, its successive volumes and corresponding pressures are thus known, and the successive products of the volume and the pressure are the same.

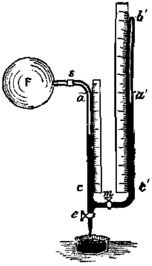

FIG. 27

For pressures above that of the atmosphere the mercury is made to stand at the level *cc'* before the flask F is screwed on, and more mercury is poured in at *b'* to obtain the increased pressure; the rise in *ac* is of course less than that in *b'c'*.

42. Application of Boyle's Law to a Mixture of Gases.—Suppose a mass of air to be enclosed in a vessel whose volume is V and let the pressure of the gas be P_1. If more air be forced into the vessel the volume occupied by the larger quantity is V, but the pressure P_2 must be greater than before. The quantity of air that was added also itself "fills" the whole vessel and increases the previous pressure by an amount equal to the pressure which this portion itself would have exerted had it alone occupied the whole volume V. And provided that the gases obey Boyle's law and do not act chemically on each other, it is indifferent whether the masses of gas thus mixed are of the same or of different kinds.

Quantities of gases whose volumes and pressures are respectively V_1P_1, $V_1'P_1'$,

and $V_1''P_1''$ are forced into a vessel whose volume is V_2, required to find the final pressure P.

$$\text{For the first gas only } P_2V_2 = P_1V_1; \quad \therefore P_2 = \frac{1}{V_2}(P_1V_1).$$

$$\text{For the second only } P_2'V_2 = P_1'V_1'; \quad \therefore P_2' = \frac{1}{V_2}(P_1'V_1').$$

$$\text{For the third only } P_2''V_2 = P_1''V_1''; \quad \therefore P_2'' = \frac{1}{V_2}(P_1''V_1'').$$

$$\therefore P = P_2 + P_2' + P_2'' = \frac{1}{V_2}(P_1V_1 + P_1'V_1' + P_1''V_1'').$$

43. LIMITATIONS OF BOYLE'S LAW.—Boyle's law was long accepted as perfectly exact and equally applicable to all gases, until Despretz, by enclosing gases in small tubes dipping in mercury on which very strong pressure was exerted by a screw, found that the surfaces of the mercury in the tubes which were at the same height at low pressures, were at unequal heights at high pressures. As the pressure increased, carbonic acid, sulphuretted hydrogen, and ammonia diminished in volume at a greater rate than air, while hydrogen differed from air in the opposite direction. The relation between the volume and pressure was different for each gas, so that clearly Boyle's law did not apply to them all. Fig. 28 shows the apparatus introduced by Pouillet for the convenient demonstration of these facts.

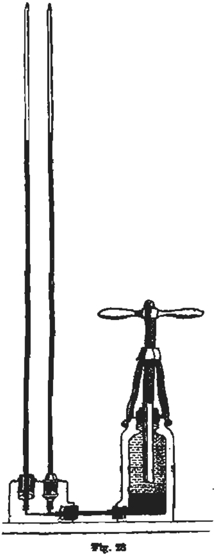

Fig. 28

Dulong and Arago afterwards experimented on air by means of a very tall Boyle's tube. The mercury was forced in at the bend of the tube by a pump, and the volume of the air in the short arm was read at intervals as the mercury in the long arm gradually rose to a height of about 60 ft. The results did not indicate any departure from Boyle's law. Such an apparatus, however, possesses for this purpose a

fundamental fault. Errors in measuring the heights of the columns are unavoidable, and one is as liable to make an error of say ·3 mm. in reading a column ·05 m. high, as in reading one of 1 m. high. As, then, the air enclosed in the short arm diminishes in volume the unavoidable errors bear a constantly increasing ratio to the quantity measured, and in this case the errors were sufficiently great to entirely conceal any deviation from Boyle's law.

44. **Regnault's Experiments on Boyle's Law.**—For moderate pressures Regnault ascertained the extent of the deviation with extreme accuracy. The more essential portion of his apparatus is shown in fig. 29, in which AOO represents the Boyle's tube. The arm A, open to the atmosphere, was about 30 m. high, and the arm B, which was closed at the top by the tap O, was 3 m. high. The lower portion of the tube AOO contained mercury, of which any amount that was required could by means of the pump G be forced into the tube when the tap F was opened. The arm OB was most carefully gauged and graduated, and elaborate means were taken for the accurate measurement of the height of the mercury column in A. By opening the tap O the tube B could be placed in communication with a reservoir D, containing the gas to be experimented on, which, after having been carefully dried, was forced into the reservoir along the tube E by means of a pump until the pressure in D reached any desired value.

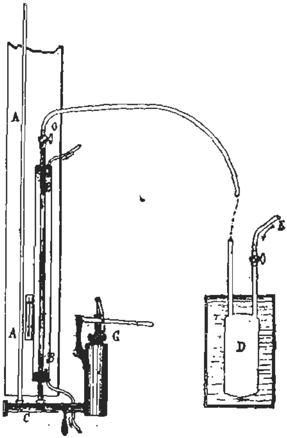

Fig. 29

The reservoir D being full of gas and the tube B of mercury, the tap O was opened and the gas admitted into the tube B until the mercury stood at the level of the point marked *a*. The tap O was

then closed, and the height of the mercury in A was observed. The tap F was then opened, and by means of the pump G mercury was forced into the tube C until it stood nearly at a point *c*, halfway up the tube B. The tap F was then closed. The mercury of course had simultaneously mounted in the tube A, and its height was again observed as well as the exact height in B.

The tube B and the reservoir D were each surrounded by a vessel of water maintained at a constant temperature.

In each case the pressure in the reservoir D was first adjusted to the required value, and the gas then admitted into the tube B. The volume was then reduced to one-half of the original value. Thus all the measurements, whether at high or low pressures, were made under the same conditions, and were equally exact.

If Boyle's law were rigorously true the expression V_1P_1/V_2P_2 (where V_1V_2 represent initial and final volumes and P_1P_2 initial and final pressures) would be always equal to *unity*. This was never the case. For example, when P_1 and P_2 were equal to the pressure of 1 and of 10 m. of mercury respectively, Regnault obtained for this ratio the following values:—

	Air.	Nitrogen.	Carbonic Acid.	Hydrogen.
$\frac{V_1P_1}{V_2P_2}$	1·0067	1·0057	1·1649	·9921

These results show that for no known gas is Boyle's law rigorously true, that the amount of deviation from it is different for each gas, and that in the case of hydrogen the deviation is in the opposite direction to that of the other gases tried. With air, nitrogen, and carbonic acid, since the initial product is greater than the final, we see that as the pressure is increased the volume decreases at a rate faster than that indicated by Boyle and Mariotte's law. This statement holds for values of the pressure up to about 75 atmospheres (see Art. 120).

45. Boyle's Law at High Temperatures.—*All the above experiments took place at ordinary temperatures. Experiments by Amagat at temperatures between 100° and 320° showed that sulphurous acid and carbonic acid depart much less from Boyle's law at high than at low temperatures. There is thus reason to think that at temperatures sufficiently high above their boiling-points all gases would tend to behave as hydrogen does.*

46. A PERFECT GAS.—The deviations of the more permanent gases—*e.g.* oxygen, hydrogen, nitrogen, carbonic oxide—from Boyle's

law are extremely small under ordinary circumstances. It is, therefore, usual in practice to regard the law as strictly applicable to them. In reality, however, the law is only rigidly applicable to an imaginary gas, which is often alluded to as a **perfect gas**.

47. RELATION BETWEEN VOLUME V AND TEMPERATURE T WHEN THE PRESSURE P IS CONSTANT. CHARLES' OR GAY-LUSSAC'S LAW.—*Charles first remarked* that the rate of expansion of all gases is the same; but this law was *first published by Dalton and Gay-Lussac. In Gay-Lussac's investigations* the gas to be experimented on, having been thoroughly dried, was enclosed in a thermometer tube having a spherical bulb A of

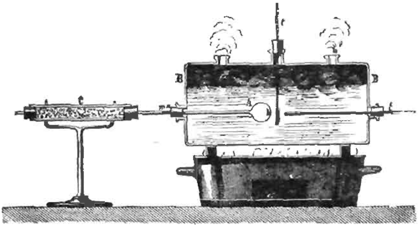

Fig 30

known capacity (fig. 30) and a long stem which was accurately calibrated and graduated and open at the end. The enclosed gas was confined by a short column of mercury *mn*, and since the tube was open the pressure of the gas during the experiment was always equal to that of the atmosphere. The tube was placed horizontally in a bath, and the bath being first filled with melting ice, the tube was adjusted, so that all the confined air was inside the bath, and therefore all at the required temperature. The temperature of the bath was then raised, and as the pellet of mercury was pushed out by the expanding air, the volume occupied by the gas at successive temperatures was observed. Gay-Lussac tried air, oxygen, nitrogen, and hydrogen at different pressures, and, as the result, enunciated the law that *all gases when heated expand at the same rate, and the coefficient of expansion is independent of the pressure.* This is Gay-Lussac's or Charles' law. If a be the coefficient of

expansion, then for any gas whose volume is V_0 at 0° C. and V_τ at τ° C.

$$V_\tau = V_0 (1 + a\tau).$$

When corrected for the expansion of the glass, Gay-Lussac obtained, as the mean coefficient of expansion of gases between 0° and 100° C., the value ·00375; but we now know that this value is too great— the correct coefficient being for Centigrade degrees ·00367. The causes of error were that gas is liable to leak between the column of mercury and the glass, since mercury does not wet glass; and that sufficient precautions were not taken to dry the tube. Experiments undertaken by Rudberg showed that the latter condition was difficult of fulfilment, and if not fulfilled, greatly disturbed the results of the experiments.

48. **Regnault's Method.**—Regnault's apparatus is shown in fig. 31. The gas to be experimented on was contained in a glass globe B that communicated by a narrow tube with a manometer MM′. A tube I, communicating with the tube CD, served to introduce the gas, and to adjust its pressure to any required value. The reservoir B was surrounded by a metallic vessel E, by means of which the temperature of B could be adjusted. The manometer MM′ was also contained within a vessel that was kept full of water at a constant temperature τ.

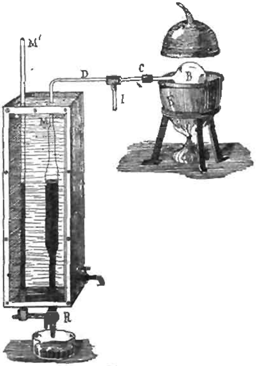

Fig. 31

Great care was taken to dry the globe B, the communicating tubes, and the gas itself. The gas was introduced into B, while the vessel E was filled with melting ice. At this stage of the operation the mercury was made to stand at the same height in the two tubes MM′, and the gas in B was therefore at the atmospheric pressure P_0.

The globe B was then surrounded by steam from water caused to boil in the vessel E, and as the gas expanded the mercury was forced down the branch M and up the branch M′. By turning the tap R mercury was drawn off until the level of the surfaces was again the same.

The volume of the globe and of each portion of the tubes occupied by the gas had been carefully determined beforehand.

Let V be the volume of the globe B and a the coefficient of expansion to be found, then, neglecting the expansion of the glass and supposing that the atmospheric pressure remained at the standard value throughout the experiment, we have—

(i) Initially, a volume of gas V at 0° and a volume V_1 contained within M at τ°; the total volume reduced to 0° C. is thus

$$V + \frac{V_1}{1 + a\tau}.$$

(*ii*) Finally, a volume of gas V at a temperature 100° C. and a volume V_2 contained within M at a temperature τ° C.; the total volume reduced to 0° C. is thus

$$\frac{V}{1 + 100a} + \frac{V_2}{1 + a\tau}.$$

And these reduced volumes are equal.

$$\therefore V + \frac{V_1}{1 + a\tau} = \frac{V}{1 + 100a} + \frac{V_2}{1 + a\tau},$$

an expression in which the only unknown quantity is a.

Regnault corrected his result for deviations from the standard atmospheric pressure and for the expansion of the glass vessel The final value obtained for air was ·00367 or 1/273.

49. Weight Thermometer Method.—The following method is instructive and easily practicable. Let a large weight thermometer, whose weight is accurately known, be carefully dried, filled with dry air, and placed with its mouth under mercury. Let the bulb be then immersed in steam from boiling water; the rise of temperature is accompanied by expansion, and air is forced out. When this process is complete allow the thermometer to cool with its mouth still under the mercury, and complete the cooling by surrounding the bulb with melting ice. The contraction of the air is accompanied by the passage of mercury into the bulb, and when the cooling is complete the thermometer is taken out, carefully

dried, and again weighed. The mass of mercury within it is thus known: let it be m_1. The instrument is then completely filled with mercury and allowed to cool to 0° C. with its mouth under mercury. It is then again weighed, and the mass of mercury that exactly fills the apparatus at 0° C. is thus known: let it be m_2.

Then, neglecting the expansion of the glass, m_2 is proportional to, and may be taken to represent, the volume of a certain mass of air at the boiling-point of water, and $m_2 - m_1$ the volume of the same mass of air at the freezing-point. If the boiling-point be taken as exactly 100°,

$$\frac{1 + 100a}{1} = \frac{m_2}{m_2 - m_1}.$$

Thus if the mass of the thermometer itself be 5 grm., that of the thermometer and the mercury which entered on cooling 15 grm., and that of the thermometer *quite full of mercury 42·3 grm., then, neglecting the expansion of the glass,* 42·3 − 5, *i.e.* 37·3 *units, may be taken as the volume of the interior,* and 42·3 − 15, i.e. 27·3 units, that of the air which remained after some had been expelled.

Thus 27·3 volumes at 0° become 37·3 volumes at 100°. and

$$1 + 100a = \frac{373}{273} = 1 + \frac{100}{273},$$

$$\text{whence } a = \frac{1}{273}.$$

50. RELATION BETWEEN THE TEMPERATURE T AND THE PRESSURE P WHEN THE VOLUME V IS CONSTANT.—Regnault's apparatus for the determination of this relation is shown in fig. 32, the general arrangement and method of procedure being the same as that indicated in Art. 48.

The main point of difference was that the gas in the globe B was not allowed to expand, mercury being poured in at M′ in just sufficient quantities to keep the surface at the mark *b* as the pressure increased. As no large quantity of air was contained within M it was not necessary to place the manometer in a bath.

The space around B was first filled with ice, and by pouring mercury in at M′ or drawing it off at R as required the level was adjusted to the fixed mark *b*. When the temperature of B was raised to boiling-point the mercury surface stood at some higher level such as the point *e*.

Thus a certain mass of gas was made to occupy the same volume at 0° as at the boiling-point, and the difference of the pressures to which it was subjected in the two cases was a quantity p measured by the height of the mercury column $b'e$. Then if P

is the height of the barometer (supposed constant and at its standard value), the pressure at 0° C. is to the pressure at 100° C. as P is to $P + p$; and taking a' as the coefficient sought, τ, V and V_1 with the same meanings as in Art. 48, and V_2 equal to V_1, we have

$$P\left\{V + \frac{V_1}{1 + a'\tau}\right\} = \left(P + p\right)\left\{\frac{V}{1 + 100a'} + \frac{V_1}{1 + a'\tau}\right\}$$

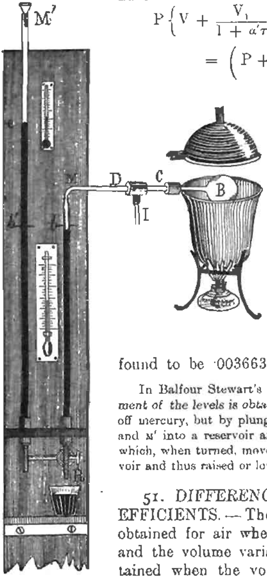

Fig. 32

and the value of a' in the small quantity $\frac{V_1}{1 + a'\tau}$ may be taken as that obtained in Art. 48. Care was taken to obtain the exact temperature of B, which was not precisely 100°. Correction was also made for the expansion of the globe B. The final result was that for air the coefficient of increase of pressure with temperature was found to be ·003663.

In Balfour Stewart's form of this apparatus the adjustment of the levels is obtained, not by pouring in or drawing off mercury, but by plunging the lower ends of the tubes M and M' into a reservoir and replacing the tap R by a screw, which, when turned, moved a plunger in or out of the reservoir and thus raised or lowered the mercury.

51. *DIFFERENCE BETWEEN THE COEFFICIENTS.* — The value of the coefficient a obtained for air when the pressure was constant and the volume variable was ·0036706; that obtained when the volume was constant and the pressure variable was ·003663. That they are not exactly the same is due to the fact that the gases do not rigorously obey Boyle's law. In one case the gas expands, in the other it does not; and since with expanding air the volume increases faster than the pressure decreases, the coefficient connect-

ing temperature and volume would necessarily be greater than that *connecting temperature and pressure.* If Boyle's law were exactly true the coefficients would be exactly the same.

52. GASES OTHER THAN AIR.—Regnault investigated the behaviour of many gases and found that the law of equal dilatation was only true for the more permanent gases. For gases more easily capable of liquefaction the coefficients of expansion differed considerably from the value $\frac{1}{273}$. For example, the coefficients for cyanogen were found to be ·003829 at constant volume and ·003877 at constant pressure.

53. THE AIR THERMOMETER.—The rate of expansion of air with rise of temperature is such that 273 c.cm. at 0° C. become 373 c.cm. at 100° C. If, then, air be used as a thermometric substance, it is most convenient, in order that the degrees may be the same as those of the Centigrade thermometer, to call 0° C. and 100° C. respectively 273° and 373° on the air thermometer. Any Centigrade reading is converted into a reading on the air thermometer scale by adding 273; thus 45° C. and −37° C. correspond respectively to 318° and 236°. On account of the very close agreement of this scale with that described in Chap. xxvi, temperatures expressed on the air thermometer are often called **absolute temperatures**; and −273° C., which would give theoretically a volume zero for any mass of air, is called the absolute zero of temperature. We shall always write θ for absolute temperatures.

54. COMBINATION OF THE GASEOUS LAWS.—If temperature be measured on the absolute scale, the law of Gay-Lussac or Charles takes the following simple form: *The volume of any mass of gas is proportional to its absolute temperature.* Since, then, V is proportional to θ, and to $\frac{1}{P}$ (Boyle's law), $V \propto \frac{\theta}{P}$, and $\frac{VP}{\theta}$ is constant for the same mass of gas. When the volume, pressure, and temperature of a mass of gas all change together

$$\frac{V_1P_1}{\theta_1} = \frac{V_2P_2}{\theta_2} = \text{a constant R},$$

the suffixes $_1$ and $_2$ indicating, as before, initial and final values.

55. THE DENSITY OF DRY AIR.—It is often requisite to know the density, i.e. the mass of unit volume, of air. At the standard temperature 0° C., and 760 mm. of mercury pressure, the

mass of 1 c.cm. has been found to be ·001293 grm.; hence at absolute temperature θ and pressure P the mass of 1 c.cm. of air is

$$\rho = \cdot 001293 \times \frac{273}{\theta} \times \frac{P}{760}, \quad = \cdot 0004644 \frac{P}{\theta} \text{ grm.}$$

56. EXAMPLES.

1. In a vessel whose capacity is 8 litres are placed 16 l. of hydrogen originally at 120 mm. pressure, 5 l. of carbonic acid at 360 mm., 20 l. of nitrogen at 700 mm., and 2 l. of oxygen at 500 mm. pressure. Find the pressure of the mixed gases.

$$\begin{aligned} \text{Hydrogen pressure} &= \tfrac{1}{8} \times 16 \times 120, \\ \text{Carbonic acid} \quad ,, &= \tfrac{1}{8} \times 5 \times 360, \\ \text{Nitrogen} \quad ,, &= \tfrac{1}{8} \times 20 \times 700, \\ \text{Oxygen} \quad ,, &= \tfrac{1}{8} \times 2 \times 500, \\ \therefore \text{Total pressure P} &= \tfrac{1}{8} \times 10(192 + 180 + 1400 + 100) \\ &= 2340 \text{ mm. of mercury.} \end{aligned}$$

2. A barometer tube of uniform bore is 34 in. long. A small quantity of air is left in the tube above the mercury, so that the barometer registers 30 in. when the true atmospheric pressure is 30·05 in. What will be the true barometric reading when this barometer registers 28 in.?

(1) Initially the volume V_1 of the enclosed air is 4 units; the pressure P_1 is the difference between that of the atmosphere and that of the actual mercury column, i.e. 30·05 − 30 = ·05.

(2) Finally, the volume V_2 is 6 units, and the pressure P_2 is unknown.

$$\begin{aligned} V_1P_1 &= V_2P_2, \\ 4 \times \cdot 05 &= 6P_2, \\ \therefore P_2 &= \cdot 0\dot{3}. \end{aligned}$$

The pressure of the air enclosed is thus $\cdot 0\dot{3}$ in. of mercury. This pressure added to that of the mercury column is equal to the atmospheric pressure, which is therefore $28 \cdot 0\dot{3}$ in.

3. A glass vessel contains 8 litres of nitrogen at 0° C. and 760 mm. pressure; the temperature is raised to 15° C. and the pressure decreased to 750 mm.; what mass of nitrogen will escape? [1 c.cm. of nitrogen at 0° and 760 mm. weighs ·00125 grm.; c. coeff. of glass = ·000025.]

(1) Initially the 8 l., i.e. 8000 c.cm., weigh

$$8 \times 1 \cdot 25 = 10 \text{ grm.}$$

(2) Finally, the volume of the vessel, and therefore of the nitrogen, is

$$8\{1 + 15(\cdot 000025)\} = 8 \cdot 003 \text{ l.}$$

At 15° and 750 mm. pressure 1 c.cm. of nitrogen weighs

$$\cdot 00125 \times \frac{75}{76} \times \frac{273}{288} \text{ grm.};$$

$$\begin{aligned} \therefore 8 \cdot 003 \text{ l. weigh } 8 \cdot 003 \times 1 \cdot 25 \times \frac{75}{76} \times \frac{273}{288} \text{ grm.} \\ = 10 \cdot 00375 \times \cdot 935 \\ = 9 \cdot 3535 \text{ grm.} \end{aligned}$$

(3) ∴ Mass expelled = 10 − 9·3535 = ·6465 grm.

4. A piece of iron measuring 1000 c.cm. is weighed at 0° C. and again at 100° C. What will be its apparent change in weight?

Coefficient of expansion of air	=	·00367.
" " " iron (linear)	=	·000012.
Mass of 1000 c.cm. of air at 0°	=	1·293 grm.

The change of weight is due to a change in the weight of the air displaced.

(1) At 0° C. volume of air displaced = 1000 c.cm.
" weight " " = 1·293 grm.

(2) At 100° C. volume of air displaced = 1000{1 + 100(3 × ·000012)}
= 1003·6 c.cm.

At 100° C. 1 c.cm. of air weighs ·001293 ÷ {1 + 100(·00367)} grm.
= ·001293 ÷ 1·367 grm.

∴ Weight of 1003·6 c.cm. = 1003·6 × ·001293 ÷ 1·367
= ·9493 grm.

∴ Increase of weight = 1·293 − ·9493 = ·3437 grm.

QUESTIONS AND EXERCISES

1. Describe a method of finding the coefficient of increase of elasticity of a mass of air occupying a constant volume.
2. A hundred cubic inches of air weigh 31 gr. when the temperature is 0° C. What will be the weight of the same volume of air when the temperature is 20° C., and the pressure one-third of its original amount, the coefficient of expansion being 11/3000?
3. State concisely the characteristic properties of permanent gases, and sketch an apparatus for determining their coefficient of expansion at constant volume.
4. A quantity of oxygen gas occupies 500 c.cm. at 20° C. What will be its volume at 40° C., the pressure remaining constant? (The coefficient of expansion for oxygen is 11/3000.)
5. A quantity of gas occupies 3000 c.cm. at 273° C. and 760 mm. pressure; find the volume at 750 mm. pressure if the temperature remain unchanged. Also find the volume of the gas if the pressure remain at 760 mm. and the temperature fall to 0° C.
6. A quantity of gas occupies 580 c.cm. at 17° C. and 780 mm. pressure. What would be its volume (*a*) at 30° if the pressure remain constant? and (*b*) at 30° and 760 mm. pressure?
7. A quantity of air occupies 10 c. ft. at 0° C. and under a pressure of 20 in. of mercury. What will be its volume at 30° C. under a pressure of 1200 in. of mercury?
8. A cubic foot of dry air weighs 540 gr. when the thermometer is at 14° C. and the barometer at 30 in. Show that an equal volume of air will weigh about 535 gr. when the thermometer is at 7° C. and the barometer at 29 in.
9. A thousand cubic inches of air at 30° C. are cooled to 0° C., and at the same time the external pressure upon the air is doubled. To what is the volume reduced, the coefficient of expansion of air for 1° C. being ·00366?
10. Describe Regnault's experiments and apparatus to determine the coefficient of expansion of a mass of air under constant pressure, and state the conclusions

which he drew from the fact that it differs from the coefficient of increase of elasticity under constant volume.

11. The readings of a true barometer and of a barometer which contains a small quantity of air in the upper portion of the tube are respectively 30 and 28 in. When both barometers are placed under the receiver of an air-pump from which the air is partially exhausted, the readings are 15 and 14·5 in. respectively. Find the length of the tube of the faulty barometer measured from the surface of the mercury in the basin.
12. A closed exhausted brass vessel weighs 3 kg. in air and holds exactly 20 l. at 0° C. How much would it weigh *in vacuo* when filled with water at 50° C.?
13. A cubic metre of air at 0° C. and 760 mm. pressure weighs 1293 grm. What is the volume occupied by 50 grm. of air at 20° C. and 400 mm. pressure?

CHAPTER VI

REMARKS ON EXPANSION

57. COMPARISON OF SOLIDS, LIQUIDS, AND GASES.—It is an almost universal rule that gases expand more than liquids and liquids more than solids—a fact, doubtless, to be attributed to the general differences of molecular condition prevailing in the three states. In solids and liquids the molecular forces offer strong resistance to change of volume however it may be effected. Thus, for instance, to lengthen an iron bar by mechanical means to the same extent as would take place if the bar were heated from 0° to 100° would require a tension of from 13 tons to 15 tons per square inch of section. The mechanical force necessary to effect or to prevent change of volume in liquids is less than that required for solids as a rule, and their resistance to expansion under heat is also less.

The molecular condition of gases is evidently very different from that of solids and liquids, and we have the remarkable contrast that, whereas each liquid and solid has a special rate of expansion peculiar to itself, all gases expand approximately at the same rate.

It is worthy of remark that the coefficients of similarly constituted bodies when not the same are of the same order of magnitude. Thus we have for

Solid metals, coefficients varying from ·000026 to ·000094.
Mercury, a liquid metal, has a coefficient ·00018.
Liquid non-metals, coefficients varying from ·0008 to ·0015.
Gases, coefficients all about ·00366.

Another interesting point shown by the tables of coefficients

concerns the range of variation. Solids differ from each other in regard to expansibility more than liquids, and liquids more than gases. There is thus an appearance of a gradual obliteration of differences as the gaseous state is approached.

58. On comparing the coefficients of the metals it appears that the rates of expansion of these substances are connected with the distance they are removed from their melting-points. Thus we have, for example:—

	Platinum.	Iron.	Copper.	Gold.	Silver.	Zinc.	Lead.	Tin.
Melting-point	1775	1600	1054	1045	954	412	326	230
Expansion coefficient at ordinary temperature for 100° C.	·00088	·0012	·0017	·0015	·0019	·0029	·0028	·0020

These eight metals form roughly three groups, indicating broadly that in metals a high melting-point is connected with a small coefficient of expansion at ordinary temperatures and a low melting-point with a larger coefficient. Some recent observations by Lemeray on sixteen metals indicated that if z be the coefficient of linear expansion and θ the absolute temperature of the melting-point, the product $z\theta$ was approximately constant.

A similar remark applies to liquids. Those which boil at a high temperature expand less when heated from 0° to 1° than those which boil at a lower temperature.

59. VARIATION OF EXPANSION WITH THE TEMPERATURE.—Experiment also shows that in both liquids and solids the process of expansion becomes more rapid as the temperature of the substance rises towards that value at which a change of physical condition takes place. For iron Dulong and Petit found the following results:—

Volume at 0° C.	Volume at 100° C.	Volume at 300° C.
100000	100355	101321

From these figures it is seen that a rise of temperature of 100° C. led to an increase of volume represented by 355 units, whereas a rise of 300° C. led to an increase of 1321 units, the latter number being much more than three times the former. So Regnault in his classic experiments on mercury found—

Volume at 0° C.	Volume at 100° C.	Volume at 300° C.
1	1·01815	1·05597

These results are typical. In solid metals a rise of temperature from 200° to 300° is accompanied by a greater expansion than a rise of temperature from 100° to 200°, and generally the rate of expansion of solids and liquids is greater at high than at low temperatures.

60. EXPANSION OF SUPERHEATED LIQUIDS.—The coefficient of expansion of liquids increases with rise of temperature up to boiling-point, and the coefficient of the resulting vapour is considerably greater still. If the liquid be heated above "boiling-point" without being allowed to vaporize the coefficient continues to increase, and may even surpass that of the corresponding vapour. Thus Thilorier found that liquid carbonic acid, when raised in temperature from 0° to 30°, increased in volume at a rate four times as great as that of air. Drion and Hirn have obtained similar results with several other liquids—*e.g.*, the rate of expansion of water at 180° is about half that of air, while liquid alcohol at 160° expands five times as fast as air.

61. TRUE COEFFICIENT OF EXPANSION.—From the preceding remarks it is clear that the value of the mean coefficient of expansion defined in Art. 12 must vary with the limits of temperature between which it is determined. If, then, it is required to calculate exactly the change that takes place in the volume of a solid or liquid, say between 19° and 20°, the use of a mean coefficient between wide temperature limits will not give very accurate results.

The form of expression for a mean coefficient of expansion is $\frac{1}{V_0} \cdot \frac{V_2 - V_1}{\tau_2 - \tau_1}$, where $V_2 - V_1$ represents the change of volume corresponding to a temperature change $\tau_2 - \tau_1$, and V_0 is the volume at 0° C. In this expression the second factor is variable. Suppose τ_2 to be one degree above τ_1, then the expression represents a mean coefficient of expansion between two temperatures only one degree apart, and in practice this is what is meant by a *true coefficient of expansion.*

Theoretically, the temperature interval $\tau_2 - \tau_1$ should be infinitely small. A true coefficient of expansion at $\tau°$ is the limiting value of the expression $\frac{1}{V_0} \cdot \frac{V_2 - V_1}{\tau_2 - \tau_1}$ when $\tau_2 - \tau_1$ each differ only infinitesimally from τ. There is thus a true coefficient of expansion for every temperature, representing the rate at which expansion is taking place at that particular temperature. The true coefficients of mercury are approximately:—

At 0°.	At 100°.	At 300°.
·000179	·000184	·000194.

Hence it is clear that the expression $V_\tau = V_0(1 + y\tau)$ does not accurately represent the relation between the volumes at τ° C. and at 0° C. The expression $1 + y\tau$ must be replaced by a converging series of the form $1 + y_1\tau + y_2\tau^2$, &c. Of this series it is usually sufficient to take three or at most four terms. Thus we have in more complete form $V_\tau = V_0(1 + y_1\tau + y_2\tau^2)$.

By means of such formulæ, when the coefficients y_1, y_2, &c., have been correctly ascertained, the volume at any temperature may be calculated with great accuracy.

The coefficients y_1 y_2 may be roughly found in this way. Taking Regnault's figures for mercury (Art. 59), and placing their values in the formula, we have—

$$1{\cdot}01815 = 1{\cdot}0\{1 + 100y_1 + (100)^2y_2\};$$
$$1{\cdot}05597 = 1{\cdot}0\{1 + 300y_1 + (300)^2y_2\};$$

and solving these equations for y_1 and y_2, we obtain $y_1 = {\cdot}000179$ and $y_2 = {\cdot}000000025$, which are very nearly the values given by Regnault. Such particular values, obtained from two experiments only, are, however, not very correct; accurate values of y_1 and y_2 are only obtainable by using all the data given by numerous experiments and applying to them the calculus of probabilities.

Chappuis has recently made some careful measurements on the rate of expansion of mercury. He used a weight thermometer made of the special glass known as *verre dur*. The thermometer tube was over a metre long and terminated in a capillary tube. The linear expansion of the thermometer tube was first accurately determined, and then observations taken of the mass of mercury expelled at various known temperatures. He makes the coefficient y_1 above $= {\cdot}0001817$ and $y_2 = {\cdot}295 \times 10^{-8}$.

For very expansible liquids it is necessary to know more than two of the coefficients of the series. Thus, according to Pierre the rate of expansion of alcohol may be represented thus—

$$V_\tau = V_0\{1 + {\cdot}001048\tau + {\cdot}00000175\tau^2 + {\cdot}00000000134\tau^3\},$$

V_0 and V_τ being the volumes at 0° C. and τ° C. respectively.

Scheel has recently measured the expansion of platinum between the temperatures of 100° C. and − 190° C. by the method of Fizeau (Art. 17). He found that correct expression of his results required three coefficients.

62. Different specimens of the same substance often exhibit differences in their thermal properties. Glass varies so much in

quality that the coefficients of expansion of two specimens may differ by as much as 30 per cent. The coefficients of different specimens of iron may vary 10 or 20 per cent. One of the commonest causes of difference between different specimens of the same substance lies in the mode in which they have been heated and cooled. With many solids it is not the case that after heating they always return to their original volume when cooled. This fact can readily be verified by removing a common thermometer suddenly from boiling water to melting ice, when, assuming that the zero of the thermometer was previously correct, the mercury will not fall to the point previously marked as the freezing-point. A good thermometer should never be subjected to violent changes of temperature. Rapid cooling produces great internal strains in glass and the metals; time is necessary for the accomplishment of the molecular changes that take place in expansion and contraction, and if the cooling is rapid these changes may go on for weeks or months before they are completed.

Masses of metal often show different properties in different directions according to the treatment to which they have been subjected, such as hammering and rolling, and hence ensue differences in their behaviour with regard to heat.

One of the most remarkable substances in this respect is india-rubber. When not stretched this substance behaves normally, but if stretched by more than a certain force it shortens when heated *and lengthens on cooling, and within limits the greater the stretching* force the greater the contraction for a given rise of temperature.

Liquids and gases recover their original volume exactly on the reversal of any change of temperature to which they may have been *subjected.*

Crystals.—In the previous articles the substances have been assumed to be **isotropic**, i.e. to have exactly the same properties in all directions. This is always the case with liquids and gases, but not always with solids. *Crystals are examples of* **aeolotropic** *substances*; they have not exactly the same properties in all directions. In general they have three rectangular axes, called the axes of elasticity, and Fizeau called the dilatations measured along these axes the principal dilatations. The linear coefficients of expansion, which are measured by the method of Art. 17, may not be the same along these axes. Sometimes expansion along one axis is accompanied by contraction along another axis. If the coefficients of expansion along the three axes be z_1, z_2, and z_3, then unit volume at 0°C.

becomes at $\tau°$ C. $(1 + z_1\tau)(1 + z_2\tau)(1 + z_3\tau)$, which is very *approximately equal to* $1 + \tau(z_1 + z_2 + z_3)$. The cubical dilatation may be measured by the weight thermometer.

Fizeau found that between 10° C. and 70° C. iodide of silver had a negative cubical dilatation. The emerald, which crystallizes in the form of a hexagonal prism, contracts along the axis and expands in a direction perpendicular to the axis, and the coefficients are such that its cubic dilatation is positive above − 4° C. and negative below that temperature. Iceland spar behaves in a similar manner. The diamond, which belongs to the regular system, possesses a positive coefficient at ordinary temperatures. Quartz expands in one direction to about the same extent as glass, and in a perpendicular direction about twice as much.

63. With many substances it happens that within certain limits of temperature changes of structure are proceeding, so that instead of obeying the general law that expansion accompanies rise of temperature, they contract when heated and expand when cooled between these limits.

Water.—The most remarkable exception to the general rule of expansion is furnished by water. It has long been known that water contracts from 0° to about 4°, and then expands from 4° to 100°.

Temperature of Maximum Density of Water.—Despretz made a series of experiments to determine this. A cylinder of water originally at 10° suspended in a cold chamber contained four thermometers at different depths. As water cools to about 4° its density increases and the colder water falls to the bottom. When below 4° the colder water is less dense and passes to the top. Despretz saw that there must be a moment when the first of these processes is just ceasing and the second just beginning. At that moment all the thermometers register the same temperature, which is the temperature of maximum density. A careful study of the thermometers led him to the value 3·98° C.

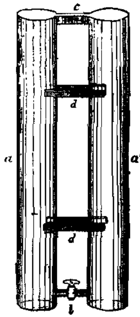

Fig. 33

Joule's method was as follows: Two vertical tubes a and a', about $4\frac{1}{2}$ ft. high and 6 in. in diameter (fig. 33), were connected at the top by a horizontal trough c, and at the

bottom by a small tube *b*. This tube was provided with a stopcock, and the trough *c* contained a light glass bead. The whole apparatus being filled with water and the stopcock closed, the temperature of the tube *a* was made higher than that of *a'*. This difference of temperature generally established a difference of density, such that on the stopcock being opened and connection established, water passed along *b* from *a'* to *a* and along *c* from *a* to *a'*, the motion being detected by the movement of the bead. If, however, the density of the water in *a* was the same as that of the water in *a'* the bead did not move. The temperature of *a* was made somewhat above 4° C. and that of *a'* somewhat below, and adjustments were slowly made as indicated in the table here quoted:—

Temperature (F.) of Warmer Tube.	Temperature (F.) of Colder Tube.	Mean.	Velocity of Current in Tube *b*.	Direction of Current.
40·959	37·363	39·161	20	Warm to cold.
40·905	37·368	39·136	8	Warm to cold.
40·711	37·317	39·014	40	Cold to warm.

The temperatures were indicated by sensitive thermometers reading to $\frac{1}{100}$ of a degree, and the above table clearly shows that the temperature sought is very nearly 39·1° F., or 3·95° C.

The temperature of maximum density of water is lowered by the presence of salt in solution. Sea water continues to contract as it cools down to its freezing-point, which is about − 4° C., and with stronger solutions the temperature of maximum density is below the freezing-point of the liquid.

Sulphur, according to Kopp, behaves in the same manner, having a maximum volume at a certain temperature. The changes in other physical and chemical characteristics which sulphur undergoes with change of temperature are well known.

In these cases it is clear that molecular changes are proceeding of a special character, such as crystallization, which mask the simple expansion that takes place in homogeneous substances. Contraction may be produced in other ways as well as by cooling, and in these exceptional cases more processes than one are in action simultaneously.

64. GRAPHICAL REPRESENTATION OF EXPANSION WITH TEMPERATURE.—The law showing the relation between volume (or length) and temperature may be conveniently

represented by a curve. Regnault recorded the results of his experiments on mercury (Art. 29) by a curve on a large copper plate.

Two lines are drawn at right angles to each other, as in fig. 34. The *point* O is called the origin and the lines OV, OT the axes. Temperatures are measured along OT, and volumes along OV. The curve O*abc* represents the expansion of alcohol. If 1000 c.cm. of alcohol at 0° be heated, the increase of volume is 54 c.cm. at 50°, 127 c.cm. at 100°, 240 c.cm. at 150°.

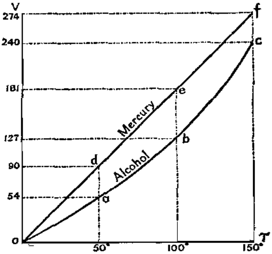

Fig. 34

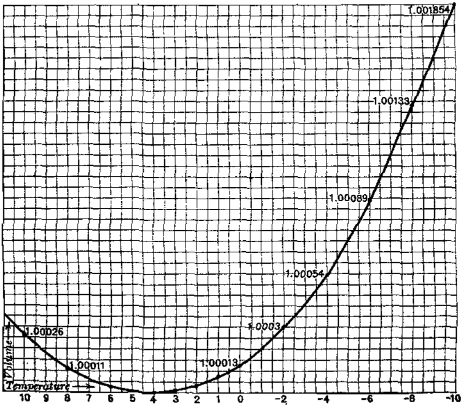

Fig. 35

Marking off a distance to indicate 50° on the axis of temperature and a distance to indicate 54 c.cm. on the axis of volumes, and drawing through these points lines parallel to the axes, the point *a* is obtained. Similarly the points *b* and *c* are fixed. Then a regular curve drawn through *Oabc* represents the relation between temperature and increase of volume. If the expansion were proportional to the temperature the line would be straight. The line *Odef* represents the curve for the expansion of 10,000 parts of mercury. It is very nearly straight, indicating that the rate of expansion of mercury with temperature is very nearly uniform.

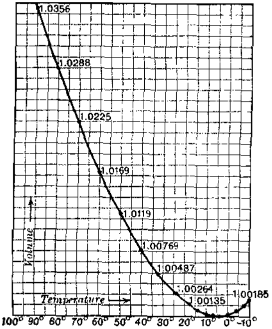

Fig. 36

In a paper by Rossetti on the expansion of water are given the results obtained by eight observers, several of whom kept the water in a liquid state below 0° C. The mean of these results is given in the following table and shown graphically in figs. 35 and 36. The rate of variation near 4° C. is seen to be very small, but not proportional to the change of temperature.

Expansion of Water

Temperature.	Volume.	Temperature.	Volume.
−10° C. ……	1·001854.	10° C. ……	1·000260.
−8° „ ……	1·001330.	14° „ ……	1·000706.
−6° „ ……	1·000892.	18° „ ……	1·001354.
−4° „ ……	1·000546.	24° „ ……	1·002644.
−2° „ ……	1·000308.	32° „ ……	1·004874.
0° „ ……	1·000130.	40° „ ……	1·007695.
1° „ ……	1·000072.	50° „ ……	1·011941.
2° „ ……	1·000032.	60° „ ……	1·016919.
3° „ ……	1·000008.	70° „ ……	1·022555.
4° „ ……	1.	80° „ ……	1·028869.
6° „ ……	1·000030.	90° „ ……	1·035675.
8° „ ……	1·000116.	100° „ ……	1·043130.

The variations of volume of water in different physical states are broadly indicated in fig. 37, but the changes are so small at one part of the diagram and so large at another part that it is impossible to draw them to scale.

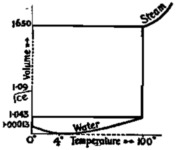

Fig. 37

65. EXAMPLES.

1. Each side of a cube of crystal has at 0° C. a length of 1 cm. If the coefficients of linear expansion of the crystal parallel to three mutually perpendicular edges of the cube are respectively ·0000083, ·0000084, ·0000047, calculate the volume of the cube at 10° C.

The precise volume at 10° C. = (1·000083) (1·000084) (1·000047),

which is very nearly equal to

$$1 + \cdot000083 + \cdot000084 + \cdot000047 = 1\cdot000214 \text{ c.cm.}$$

2. Find the reading of a mercury thermometer if the bulb and stem up to the zero graduation are exposed to a temperature of 300° C. while the remainder of the stem is at 20° C., assuming the coefficients of cubical expansion of mercury and glass to be ·00018 and ·00003 respectively.

Let the thermometer reading be $x°$, then x division-volumes of the mercury are at 20°; if they were at 300° the x divisions would occupy

$$x\{1 + 280(\cdot00015)\} = 1\cdot042 \text{ division-volume,}$$

and the thermometer would read 300°;

$$\therefore\ 1\cdot042x = 300.$$
$$x = 287\cdot9°.$$

EXERCISES

1. Compare the density of iron at 0° and 200°, given the coefficient of linear expansion = ·000012.
2. Compare the density of air at 10° C. and 750 mm. pressure with that of hydrogen at 50° C. and 1000 mm. pressure.
3. Describe the changes of volume and temperature which a pound of melting ice undergoes when heat is continually applied to it until it becomes steam.

CHAPTER VII

SPECIFIC HEAT—CALORIMETRY

66. Thus far we have been concerned chiefly with the relation between volume and temperature, and in determining by how much the volumes of different substances change when their temperature undergoes a known alteration. The quantities of heat that have been required to effect these changes have not been considered; but in the next three chapters the attention will be mainly directed to the measurement of the quantities of heat that enter or leave bodies during the operations. In this chapter we shall be concerned with the measurements of the quantity of heat which is necessary to raise the temperature of a body by a given number of degrees; and in the two following chapters, of the quantity necessary to effect change of physical condition.

67. UNIT OF HEAT.—We have no means of measuring the quantity of heat a body *contains*. To come within our cognizance heat must pass out of one body into another, and it is measured by the effect it produces on that other body in raising its temperature, in increasing its volume or its pressure, or in changing its physical condition. In order to obtain a unit by which to measure heat we have to choose which of these effects shall be taken, and then what substance and what mass of that substance shall receive the heat. Tbe effect usually chosen is change of temperature, the substance water, and the quantity unit mass. Thus **a unit of heat** is defined in general terms as *the amount of heat required to raise unit mass of water through one degree of temperature*. But, as will appear later, this is not sufficiently definite, for the quantity of heat required to effect this change varies with the temperature at which the heat enters the water (Art. 76). Hence a precise definition should state at what part of the temperature scale the change takes place. Using the gramme as the unit of mass and the Centigrade scale of temperature, *the unit of heat* (called the **gramme-degree** or **calorie**) was defined by Regnault as *the quantity of heat required to raise one gramme of water from $0°$ C. to $1°$ C.* If for one gramme we substitute one kilogramme the unit is called the *major calorie*. If the unit of mass is the pound the unit of heat is called the *pound-degree*.

Sometimes the Fahrenheit scale of temperature is used. In that case the pound-degree is five-ninths of that defined above. This scale is, however, very seldom used when the gramme is the unit of weight.

When thus defined the unit of heat is perfectly definite, but it must be added that in ordinary practice the limitation "from 0° C. to 1° C." *is not observed, and that the quantities of heat required to* raise the temperature of a mass of water from $x°$ C. to $(x + 1)°$ C., or from 0° to 1°, are taken as equal when x is any ordinary temperature. Some investigators now take the temperature rise from 15° C. to 16° C. instead of from 0° C. to 1° C. in the definition of their unit; others define the calorie as the $\frac{1}{100}$th part of the heat required to raise unit mass of water from 0° C. to 100° C. Thus the 0°, the 15°, and the mean calorie are all in use.

68. THERMAL CAPACITY.—We have in Chap. I given a qualitative idea of the meaning of this term in its general sense. The *thermal capacity of unit mass*, which means the number of units of heat required to raise the temperature of unit mass of the substance through 1° C., is called the **specific heat** of the substance. The specific heat of water is thus unity by the definition of the unit of heat.

The total thermal capacity of any mass is equal to the product of its mass by its *specific heat; this is sometimes termed the* **water-equivalent** of the body. Thus, the specific heat of brass being ·0939, the equivalent of 200 grm. of brass is 18·78 grm. of water. The quantities of heat taken in or given out by these masses during the same change of temperature are equal.

Mean Specific Heat.—The specific heat of a body is measured by determining how many units of heat are required to raise some known mass of the body through a definite range of temperature, or how many such units the body gives out in cooling through a known range of temperature.

If H represent the heat absorbed by the body, m the mass, and $\tau_2 - \tau_1$ the range of temperature, the specific heat $S = \frac{H}{m(\tau_2 - \tau_1)}$. This is called the mean specific heat between the temperatures $\tau_2°$ and $\tau_1°$. (Compare Art. 12.)

69. CALORIMETERS.—A calorimeter is an apparatus used for measuring quantities of heat. *There are many forms of calorimeters.* In all of them it is desirable that arrangements should be made to check interchange of heat between external bodies and those that are the subject of experiment. The lower part of fig. 66 shows a form suited for general work. It consists of two copper vessels CC and KK, one supported inside the other by means of some non-conducting substance, the opposite surfaces being kept brightly

polished, and each furnished with a lid through which pass a thermometer and a stirrer. In accurate work these are often enclosed in another large vessel H made of tin, and having double walls, the space between which is filled with water.

70. METHODS OF DETERMINING SPECIFIC HEAT.—We proceed to describe some of the methods by which the specific heat of a body may be determined.

A. Solids

The Method of Mixtures.—The principle of this method is to place in intimate contact known masses of different substances at different temperatures, of one of which the specific heat is known, and then to equate the loss of heat of one body with the gain of heat of the other body. Water, whose specific heat is by definition unity, is commonly taken as one of the substances. A simple experiment will illustrate the principle.

Place a pound of brass wire in boiling water (100° C.) for a few *minutes; then quickly transfer it into a pound of cold water contained* in a thin glass beaker in which stands also a good thermometer.

Suppose the water was initially at 15° C. and finally at 22·3° C. Then the brass has fallen through 77·7° (100° to 22·3°), and in doing so has parted with sufficient heat to warm the water through 7·3° (15° to 22·3°). Therefore the capacity of brass for heat is evidently $\frac{73}{777}$ of that of water; hence the specific heat of brass is ·094.

In general symbols, if m_1 be the mass of the solid, S its specific heat, and τ_1 its initial temperature; m_2 the mass of the water *(including the water-equivalent of the vessel), and* τ_2 *and* τ_3 the initial and final temperatures of the water, then we have

$$\text{Heat given out by the solid on cooling} = S \times m_1 \times (\tau_1 - \tau_3),$$
$$\text{Heat communicated to the water} = m_2(\tau_3 - \tau_2),$$
$$\text{and these are equal.} \quad \therefore S = \frac{m_2(\tau_3 - \tau_2)}{m_1(\tau_1 - \tau_3)}.$$

This method is sufficient for preliminary values to serve as a basis for more exact measurements, but it is the barest form of the experiment and would not furnish accurate results, for the following reasons: (i) Some of the heat of the wire was lost during the act of transference from the hot to the cold vessel; (ii) the wire carried hot water with it; (iii) some of the heat of the wire was not communicated to the water, but was absorbed by the beaker itself;

(iv) heat was lost by radiation from the beaker before the final temperature was read.

71. Regnault's apparatus (fig. 38) is designed to obviate these errors as far as possible. Its chief parts are a vessel C, in which the body is heated, and a calorimeter shown underneath at N. Water is boiled in a vessel V, and the steam passes into the vessel C, which consists of three concentric cylinders, through the outer two only of which the steam circulates, issuing by a tube D into a condenser.

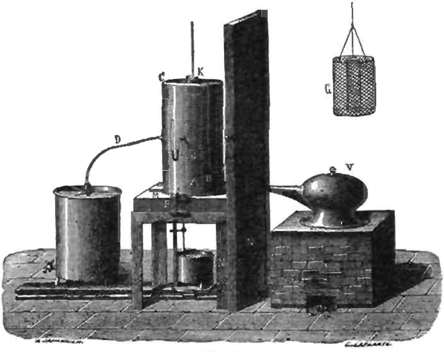

Fig. 38

The central cylinder AK is dry; it is closed at the top by a cork K and at the bottom by a sliding plate of metal E. Within this central cylinder is suspended by a thin silk thread the piece of solid G to be experimented on.

We give the details of an actual experiment on a piece of zinc weighing 185·3 grm. The calorimeter (of brass) weighed 205·3 grm.; its water-equivalent was therefore 205·3 × ·0939 = 19·28 grm. That of the thermometer placed in the calorimeter was 1·9 grm. The water within the calorimeter weighed 259·25 grm. The total mass to be raised in temperature was thus equivalent to 19·28 + 1·9 + 259·25 = 280·43 grm. of water. The zinc was left in the central cylinder for about $1\frac{1}{2}$ hour. The temperature of the room was 16·8°

and the temperature of the water in the calorimeter, as indicated by a delicate thermometer, was 14·5° C. when drawn from the tap, and was observed to rise at the rate of ·04° per minute. When the temperature of the calorimeter was 14·62°, the thermometer in AK recording 100°, the calorimeter was quickly slid into its place, E removed, K eased, the zinc let down into the water, and the calorimeter slid out of its position. The water was stirred by moving the zinc about, and the immersed thermometer was read. At the end of half a minute it had reached 18°, after one and a half minute it read 19·6°, at the end of four minutes 19·44°; and the experiment was at an end.

The result was deduced thus: Half a minute elapsed between the reading of the thermometer in the calorimeter and the immersion of the zinc; the temperature of the calorimeter was therefore 14·64. The calorimeter containing the zinc was exposed to the room for $1\frac{1}{2}$ minute. During the first half-minute its average temperature was $\frac{1}{2}(14{\cdot}64 + 18{\cdot}0) = 16{\cdot}3$, sufficiently close to the temperature of the room to render correction for radiation unnecessary. During the next minute its average temperature was $\frac{1}{2}(18 + 19{\cdot}6) = 18{\cdot}9°$, which was 2° above the room, the loss by radiation being thus sufficient to cause the thermometer to fall ·05°. The final corrected reading of the thermometer was thus 19·65° C.

The fall of 185·3 grm. of zinc through (100 − 19·65)° C. gave out heat enough to raise 280·43 grm. of water through (19·65 − 14·64)°.

$$\text{Hence } 185{\cdot}3 \times 80{\cdot}35 \times S = 280{\cdot}43 \times 5{\cdot}01$$

$$\therefore S = \frac{280{\cdot}43 \times 5{\cdot}01}{185{\cdot}3 \times 80{\cdot}35} = {\cdot}0947.$$

For general results see p. 87.

72. Specific Heat of Ice.—This was thus determined by Person. A known mass of water was put into a flask of thin copper and a delicate thermometer immersed in it. The flask was then kept for some time in a freezing mixture. When the water was frozen and the ice at a temperature considerably below 0° C., the flask was transferred to a calorimeter containing a known mass of warm water. The mercury of the thermometer immersed in the calorimeter at once began to fall and that in the ice to rise. The indications of the two thermometers gave the ratio of the thermal capacities of ice and water.

Thus, if the masses of the ice, the copper flask, and the warm water were respectively m_1, m_2, and m_3 grammes, the original and final temperatures of the ice $-\tau°$ C. and $-\tau_1°$ C., and those of the

warm water τ_2° C. and τ_3° C., then, taking ·095 for the specific heat of copper and S for that of ice, we have

Heat given out by the warm water $m_3(\tau_2 - \tau_3)$ calories,
Heat absorbed by the ice and flask $(Sm_1 + \cdot 095m_2)(\tau - \tau_1)$ calories,

and equating these values S is determined. The value obtained was ·504.

73. JOLY'S STEAM CALORIMETER.—A useful method of calorimetry has recently been worked out by J. Joly.

Fig. 39 indicates his arrangements for measuring specific heat. The substance to be experimented on is placed in one of the pans, A, of a balance, and this pan, which is made of platinum, is enclosed in a metal chamber B, and is supported by a thin platinum wire passing through a plug of plaster of paris. The equilibrium of the balance is, of course, maintained by weights placed in the other pan. Into the top of the chamber B passes a pipe from a boiler full of steam, which, when the communication is opened, rapidly fills the chamber B and passes out through a pipe at the bottom of the chamber, carrying the air with it. When the air is all driven out the exit pipe is nearly closed, and steam condenses on the pan A and on the substance which it contains. The weights which it is necessary to add to the other pan of the balance to maintain equilibrium, give the mass of the steam thus condensed. The heat given out by this steam in condensation is absorbed by the pan and the substance which it contains, while their temperature is rising from the initial to the final value—

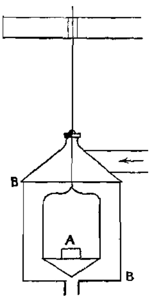

Fig. 39

Let m_1 = mass of substance in the pan A,
S = specific heat of that substance,
τ_1 and τ_2 = initial and final temperatures of A,
q = thermal capacity of the pan A,
m_2 = mass of steam condensed,
L = latent heat of the steam (Art. 113);

then Heat given out $= m_2 L$,
Heat absorbed $= (m_1 S + q)(\tau_2 - \tau_1)$,
and $m_2 L = (m_1 S + q)(\tau_2 - \tau_1)$,

whence S is determined.

The quantity q is determined by an independent experiment when there is no substance in the pan A. A correction is necessary for the hydrostatic upthrust of the steam in the chamber. To prevent condensation of steam on the supporting wire it is surrounded by a spiral of platinum wire which is heated to redness by an electric current passed through it.

74. **Specific Heat at very high Temperatures.**—In determining the specific heat of platinum between 0° and 800° C. Violle proceeded thus: One of Deville's porcelain air thermometers (Art. 193), and another porcelain vessel containing the platinum were put together into the same muffle, heated by a gas furnace. When sufficiently heated, the vessel containing the platinum was taken out and the metal therein shot into a platinum eprouvette standing in the water of the calorimeter (or straight into the water). When the eprouvette was used the time of cooling was about 15 minutes, in the other case a few seconds, but in direct plunging steam is formed, although Violle says this was of negligible quantity.

B. Liquids

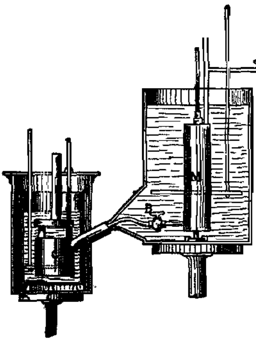

Fig. 40.

75. The method of mixtures is also applicable to liquids. The liquid whose specific heat is to be determined may be enclosed in a thin vessel, which must be, of course, allowed for as above; or we may proceed by placing in the given liquid a known mass of some suitable hot solid whose temperature and specific heat are known. (Art 82, Ex. 4.)

The apparatus shown in fig. 40 was used by Regnault. The liquid was contained in a cylinder M, standing in a bath, by means of which it was made to take

any temperature required. The vessel M was connected by a tube G with a reservoir containing air, the pressure of which was so adjusted as to force the substance in M to retain its liquid state whatever might be the temperature of the bath. By opening the stopcocks at B and G simultaneously a known mass of the liquid was forced to pass into a vessel C standing in a known mass of *water within a calorimeter. The rise of temperature of this water* gave the heat evolved. Experiments were made with many liquids through various ranges of temperature.

SPECIAL METHODS FOR LIQUIDS.—The two following methods are specially applicable for determining the specific heat of liquids.

Method of Cooling.—If a mass of warm liquid hang within an enclosure kept at some lower temperature, the liquid cools, and it is found under those circumstances (Chap. XVI) that the rate at which it loses heat is proportional to—

(i) The temperature of the warmer body.
(ii) The temperature of the enclosure.
(iii) The extent and nature of the radiating surfaces.

It is independent of the nature of the liquid.

If, then, different liquids cool at different rates *under exactly similar circumstances*, when it is known that they are emitting equal quantities of heat per second, the effect must be due to the fact that the heat radiated lowers their temperatures unequally owing to their unequal thermal capacities.

A thin copper vessel coated outside with lampblack is filled with a known weight of the liquid at a moderately high temperature, and suspended by badly conducting threads inside a large copper vessel coated inside with lampblack, which stands in a bath of water at the temperature of the room. The whole is covered by a lid through which a thermometer passes into the liquid. The time taken by the liquid to fall through a certain range of temperature is observed. The whole experiment is then repeated under the same conditions with the vessel filled exactly to the same height with water. The quantity of heat radiated in unit time by the liquid equals that similarly radiated by the water, and the equation gives the specific heat of the liquid. Thus, suppose that 28·7 grm. of a liquid whose specific heat is S cool from 55° to 25° in 18·5 minutes, while 34·5 grm. of water under exactly the same conditions take 33·25 minutes. Then the heat given out by the liquid per minute is $S \times 28{\cdot}7 \times 30 \div 18{\cdot}5 = 46{\cdot}5$ S units. And the heat given out

by the water per minute is $34 \cdot 5 \times 30 \div 33 \cdot 25 = 31 \cdot 02$ units. But these quantities are equal;

$$\therefore S = 31 \cdot 02 \div 46 \cdot 5 = \cdot 668.$$

In general symbols, if t_1 = number of seconds taken by the given liquid to cool from $\tau_1°$ C. to $\tau_2°$ C.,
t_2 = the same quantity for water,
m_1 = the mass of the given liquid,
m_2 = the mass of the water,
S = specific heat of the liquid,
A = a constant depending on the radiating surface;

then the heat given out by the liquid per second =

$$H_1 = A \times S \times m_1 \times (\tau_1 - \tau_2) \div t_1,$$

and similarly for the water

$$H_2 = A \times m_2 \times (\tau_1 - \tau_2) \div t_2,$$

and

$$H_1 = H_2;$$

$$\therefore S = \frac{t_1}{t_2} \cdot \frac{m_2}{m_1}.$$

The water-equivalent of the vessel and thermometer should be included in the values of m_1 and m_2. The method of cooling has been applied to solids, but the results obtained were unsatisfactory.

During cooling, the interior of a solid is hotter than the exterior; and as different solids have very different conducting powers, the amount of such difference of temperature would not be the same for any pair of substances. Thus the temperatures of cooling solids have no definite or comparable values. With liquids, however, convection currents are formed, and by stirring it is possible to keep the temperature of the mass very nearly constant throughout. The method is therefore applicable to liquids but not to solids.

It is better that the calorimeter should be large, have its surface blackened, and be suspended within a larger vessel which has water between its hollow walls, and is supplied with a lid of the same construction. The radiation is thereby made more uniform.

Error is liable to occur in the record of the temperature, as the temperature of a small thermometer when that temperature is rapidly changing is not accurately represented by the reading.

Electrical Method (see Chap. XIII).—The following method of comparing heat capacities is especially adapted for liquids. Two

spirals of wire constructed exactly alike, so as to have the same electrical resistance, are placed in series in an electrical circuit; the same *current flows through both, and therefore the quantities* of heat produced in the spirals are equal. If, then, these spirals are respectively immersed in equal masses of two liquids, each contained in a calorimeter, the rise of temperature produced in the liquids is inversely as their capacities for heat. The masses of the liquids need not be actually the same in practice, as any difference can be accurately allowed for in the calculations. It is necessary that the liquids should be well stirred during the experiment. To render the method applicable to liquids that conduct the electric current, Pfaundler employed spirals of glass tubing filled with mercury.

76. **Specific Heat of Water.**—One of the most careful investigations on specific heat yet made was that of Callendar and Barnes

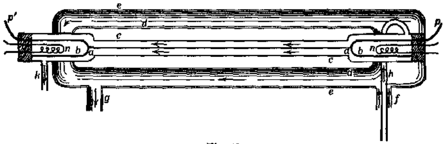

Fig. 41

on the specific heat of water. A current of electricity was passed along a thin wire contained in a tube through which a measured quantity of water was simultaneously passed. The known quantity of electrical energy developed in the wire had its equivalent in the heat communicated to the water (Art. 133), which was known in terms of its mass, rise in temperature, and specific heat.

The arrangements of the calorimeter were as indicated in fig. 41. The heating wire *a*, terminating in copper tubes *b*, was enclosed in a tube *c*. Round this inner tube *c* was a larger tube *d* which formed a vacuum jacket (Art. 122), and in turn this tube was enclosed in a water jacket *ee*. Water entering in by a pipe *f* passed continuously through the tube *e* and out by a pipe *g*. *Another stream of water* passing in by a pipe *h* flowed through the tube *c* and out by a pipe *k*. As this inner stream had previously passed through a pipe immersed in the tank which supplied the water to the jacket, the two streams of water entered the calorimeter at the same temperature. *Radiation losses were greatly reduced by the vacuum jacket.*

The temperatures of the ingoing and outflowing water were measured by platinum thermometers n and n (Art. 195) placed in the copper tubes b. The heating current entered and left by terminals pp'.

The water that flowed from k was collected and measured. Let its mass be m, and the time of flow t seconds, the thermometer readings τ_1 and τ_2, and the mean specific heat of water between these temperatures S. Then the heat developed per second was

$$\left\{\frac{m}{t} \times S \times (\tau_1 - \tau_2)\right\} + \left\{h(\tau_1 - \tau_2)\right\} \ldots\ldots\ldots\ldots\ldots (1)$$

the term $h(\tau_1 - \tau_2)$ representing the loss.

The electrical energy was measured in the following way. The same current C was maintained through the wire a and through a standard coil, and the differences of potential E_1 and E_2 between the ends of these two coils were indicated by voltmeters. Then, if r_1 and r_2 are the respective resistances of the wire a and of the standard coil, we have

$$E_1 = Cr_1 \text{ and } E_2 = Cr_2$$

$$\therefore \frac{E_1E_2}{r_2} = C^2r_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

which represents the energy developed per second in the wire a.

$$\text{Hence } \frac{E_1E_2}{Jr_2} = \left\{\frac{m}{t} \times S \times (\tau_1 - \tau_2)\right\} + \left\{h(\tau_1 - \tau_2)\right\} \ldots\ldots (3)$$

A second experiment was made, in which the value of $\frac{m}{t}$ (the rate of flow) was reduced to about one-half of the above, the current being proportionately reduced so that the rise in temperature was the same as before. Then for the second experiment also—

$$\frac{E_1'E_2'}{Jr_2} = \left\{\frac{m'}{t'} \times S \times (\tau_1 - \tau_2)\right\} \times \left\{h(\tau_1 - \tau_2)\right\} \ldots\ldots (4)$$

These two equations (3) and (4) enabled the term $h(\tau_1 - \tau_2)$, representing the heat losses, to be eliminated and S to be found.

The value obtained for S at 37·5° C. was ·99733; for temperatures between 37·5° C. and 5° C. the value was less.

C. Gases

77. TWO SPECIFIC HEATS OF GASES.—With regard to specific heat, gases present a striking contrast with liquids and solids, due to the large amount of expansion which ensues on heating. The change which solids and liquids undergo in this respect is too small to affect the values found for their specific heat, but with gases the change is far too great to be neglected. The gas must be heated and cooled during the operation of finding its specific heat, and very different results are obtained according as the gas is allowed to expand or not during the process. The simplest plan is to take a thin vessel and find how much heat is required to warm it through say 100°, first when empty, and again when full of the gas; but the mass of the gas within the vessel is so small compared with the mass of the vessel itself, that the measurement is one of difficulty.

The result is called the **specific heat at constant volume.** See Chap. XXIII.

The value obtained for the specific heat when the gas is allowed to change its volume under constant pressure is called the **specific heat at constant pressure.**

Regnault's Determination of Specific Heat at Constant Pressure.—The method employed by Regnault was in principle the same as the method of mixtures.

A steady stream of hot gas under a constant pressure was passed through a calorimeter and there gave up a portion of its heat to a known quantity of water. Fig. 42 shows the apparatus employed. It consisted of four chief parts.

The gasholder R was a reservoir of 35 l. (about 1·25 c. ft.) capacity, standing in a vessel of water which was agitated by a flat ring *a*, and whose temperature was given by a thermometer T. From R the gas was passed through a continuous set of tubes and spirals *xeh* into the atmosphere.

The Heating Apparatus S.—The gas was heated by passing through a long spiral immersed in an oil bath. The oil was kept stirred by an arrangement *a'* and the temperature was read by the thermometer T'.

The Calorimeter C.—The gas was cooled by passing through a spiral immersed in cold water kept stirred by *a"* and whose temperature was read by the thermometer T".

The Regulator r.—As the gas left R, the pressure in R, and there-

fore in the tube x, was continually diminishing throughout the experiment, and it was necessary that the rate of passage of the gas should be constant. This was effected by the regulator r, in which

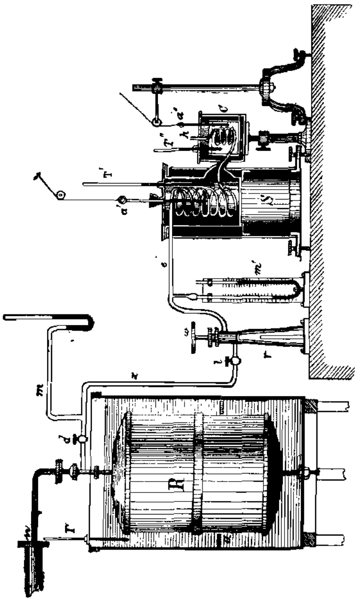

Fig. 42

the gas passed through a conical aperture into which fitted a conical plug attached to a screw w. By gradually turning up this screw as the experiment proceeded, the size of the aperture was increased, and the rate of passage of the gas maintained constant throughout,

as indicated by the manometer m', whose pressure reading was determined by the rate of flow of the gas.

Method of the Experiment.—The stopcock l being shut, the gas was compressed in the reservoir R, the bath S heated to the required temperature, and the calorimeter C filled with a known weight of water. Observations were then made as to any changes of temperature that might be proceeding in C. The gas was then allowed to pass for a suitable time, and after it had been shut off, another set of observations was made as to the changes of temperature in the calorimeter. These observations served to indicate what correction must be applied to the readings of the thermometer T″ for the effects of radiation during the progress of the heating.

The values obtained for a few gases are given in the table on page 414. The general results are—

(i) All simple gases have the same thermal capacity per unit volume.

Thus we have for the specific heats of equal volumes—

Hydrogen	·2359,	Air	·2375,
Oxygen	·2405,	Nitrogen	·2368,

which are nearly the same.

(ii) The specific heat (unit mass) of a gas does not vary with the pressure.

(iii) The specific heat of all gases increases with rise of temperature.

The specific heats of air and carbon dioxide have recently been redetermined by W. F. G. Swann by the electrical method described in Art. 76.

A steady stream of the gas was passed through a jacketed tube, and during its passage was heated by a coil of hot platinum wire through which a current of electricity was passing. The temperature of the gas as it entered and left the tube was read by two platinum thermometers. The rate of flow of the gas was determined by passing it through a number of fine metal tubes in parallel and measuring the difference of pressure between their ends, the mean pressure, and the temperature.

The quantity of heat supplied was determined by measuring the current passing through the heating coil and the potential difference between the ends of the coil. The calculation of the results was by the method indicated in Art. 76.

The values obtained were:—

	Air.	Carbon Dioxide.
At 20° C.	·2417	·2020
At 100° C.	·2430	·2241

It will be seen that these values are somewhat higher than those of Regnault, and that in the case of carbon dioxide there is considerable increase with rise of temperature.

SPECIFIC HEAT OF GASES AT CONSTANT VOLUME.—Joly has recently measured directly the specific heat of gases at constant volume. For this purpose the apparatus was in the form shown in fig. 43, which Joly calls the differential steam calorimeter. In the steam chamber B hung two similar hollow copper spheres A and C, each suspended from one pan of a sensitive balance. The spheres were about 7 cm. in diameter, and each was provided with a "catch-water" *e*. The sphere A was empty, while C was filled with gas at a known temperature and pressure, the latter being sometimes as high as the sphere could with safety sustain. The balance being in equilibrium, steam was admitted into the chamber B, and owing to the presence of the air within C, more steam was condensed on C than on A, the excess being measured by the weights added to the upper pan of A to restore equilibrium. The calculation is in principle the same as that indicated above, correction for expansion of the sphere being of course necessary. As the two spheres are alike, this differential form of the apparatus has the

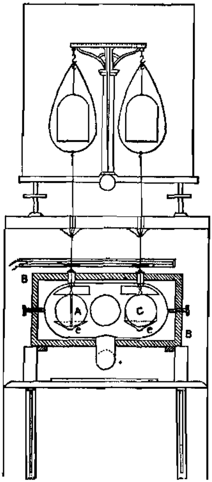

Fig. 43

advantage of eliminating corrections for the thermal capacity of the pans, and for radiation.

In one particular experiment the gas in C was air at a pressure of from 20 to 30 atmospheres, and its mass was 4·2854 grm., the thermal capacity of the gas being 6 or 8 per cent of that of the sphere.

Dr. Joly's different determinations are in close agreement with each other, and give as a mean value for the specific heat at constant volume for air ·1684 at 7·2 atmospheres pressure and ·1738 at 21·66 atmospheres pressure, for carbonic acid gas (12 atmospheres) ·0197, for hydrogen 2·35.

D. Vapours

78. Vapours are of two classes—**saturated** and **non-saturated** or superheated (Art. 98).

Regnault determined the specific heat of *non-saturated steam* at constant pressure by heating the steam to some temperature τ_1 above 100° C. and passing it into water. Let S = the mean specific heat of superheated steam between the temperatures τ_1 and τ_2, L the latent heat at τ_2, m grammes the quantity of steam used, H the number of units of heat absorbed by the calorimeter, and τ_0 its final temperature, then

The quantity of heat evolved is obtained thus:—

(i) The steam in cooling from τ_1° to τ_2° gave out $(\tau_1 - \tau_2)m$S calories.
(ii) The steam at τ_2° in condensing into water at τ_2° gave out mL calories.
(iii) The water thus formed in cooling from τ_2° to τ_0° gave out $m(\tau_2 - \tau_0)$ calories.

The quantity H is obtained from observation of the rise of temperature of the known mass of water in the calorimeter.

$$\text{Then } H = m\{S(\tau_1 - \tau_2) + L + (\tau_2 - \tau_0)\}$$

Two *experiments* with *different* values of τ_1 give two *equations* in which the unknowns are S and L, both of which are thus determined for the temperatures chosen.

The value for S obtained by Regnault between the temperature limits 225° C. and 125° C. was ·48. Perry, on examination of Regnault's results, obtains a value of about ·36 at 100° C. and ·43 at 150° C. Other determinations at higher temperatures give still higher values, approximating to ·6 when the steam is above 300° C.

Regnault also determined the specific heat of many other vapours. As the specific heat of their liquids was not unity, that quantity also

entered into the equations, as well as the latent heat of vaporization and the specific heat of the vapour. Hence three experiments were required in each case to determine the three unknown quantities. He superheated the vapours by passing them through a spiral contained in an oil bath which was maintained above their boiling-point. He found for ether ·479, for alcohol ·453, for carbon bisulphide ·157, and for chloroform ·156.

As to *saturated vapours*, suppose we have unit mass of saturated vapour at τ° C. Let its temperature be gradually raised to $(\tau + 1)^\circ$ C., and at the same time let the pressure be increased to such an extent as to keep the vapour saturated (Art. 98). Then during the increase in pressure a certain amount of work has been done on the vapour; and this work was transformed into heat. If in any case the heat-equivalent of the work done on the vapour were equal to the heat required to raise its temperature by 1°, then the vapour could rise in temperature through 1° without any other heat being supplied; i.e. its specific heat would be zero. This exact equivalence has not been found. But it has been found that with some vapours heat must be supplied independently of that resulting from the work done on the vapour, and in these cases the specific heat is, as is usual, positive. With some vapours, however, no heat has to be supplied when the temperature is raised; but, on the other hand, the heat generated by the work done as the pressure is increased is greater than that required to warm the vapour. In this case the specific heat is negative: the vapour gives out heat when its temperature is raised. The specific heat of saturated steam is a negative quantity, while that of saturated ether vapour is a positive quantity.

An experiment was devised by Hirn to test the behaviour of steam in this respect. He passed steam gently from a boiler, where it was generated under a pressure of 5 atmospheres, through a long copper cylinder the ends of which consisted of plates of glass, until all the air was expelled. The admission and exit valves were then closed, and the cylinder was full of dry saturated steam. On opening an exit valve a dense cloud appeared in the cylinder, which before had been full of perfectly transparent vapour.

79. CIRCUMSTANCES INFLUENCING THE SPECIFIC HEAT OF BODIES.—The specific heat of a body depends primarily upon the kind of matter of which it is composed, but the values obtained with different specimens of the same substance may vary considerably according to their purity. The value obtained for the specific heat also depends upon the physical condition of the body,

whether solid, liquid, or gaseous; upon the molecular condition, whether *crystalline* or *amorphous*; upon the *density*; and upon the temperature at which the observation is made.

(*a*) **Temperature: Mean and True Specific Heats.**—It is a general rule that the specific heats of solids and liquids are greater at high than at low temperatures—a fact most probably connected with that enunciated in Art. 59, viz. that the rate of expansion is greater at high than at low temperatures, one of the chief things the heat is doing being to effect that expansion against the resistance of the intermolecular forces.

A distinction has, therefore, to be drawn between **mean specific heat** and **true specific heat** analogous to that drawn between mean and true coefficients of expansion in Art. 61. The true specific heat is different for each temperature. The values given in Art. 80 are mean values within a certain range of temperature.

If S_0 and S_τ be the true values of the specific heat at 0° C. and $\tau°$ respectively, and a the quantity by which this amount increases for each degree; then the true specific heat at $\tau°$ is $S_0 + a\tau$, and the mean specific heat between 0° and $\tau°$ is $S_0 + \frac{a\tau}{2}$.

Dulong and Petit found for the values of the mean specific heat of iron—

(*a*) Between 0° C. and 100° C. ... ·1088.
(*b*) Between 0° C. and 300° C. ... ·1218.

$$\begin{aligned} \text{Hence, for iron } S_0 + 50a &= \cdot 1088 \\ \text{and } S_0 + 150a &= \cdot 1218; \\ \therefore a &= \cdot 00013 \\ \text{and } S_0 &= \cdot 1023; \end{aligned}$$

which gives for iron, $S_\tau = \cdot 1023 + \cdot 00013\tau$.

This expression is, however, not to be relied on beyond the temperature limits within which the experiments were made, as may be seen from the following values for the specific heat of iron at various temperatures which have recently been obtained—

Approximate mean temperature	1100° C.	850° C.	200° C.	50° C.	−82° C.
Specific heat	·1534	·1647	·1175	·1138	·095

These results show, besides a large variation with temperature, the existence of a maximum value at about 850° C. A similar maximum value has been found for nickel at about 300° C.

Some metals show only a small change. Thus, for example, recent determinations of the specific heats of lead and tin near their melting-point, and of gold at very low temperatures, have given values very close to those given by Regnault for ordinary temperatures (p. 87).

Among the metals whose specific heat varies least with temperature is platinum, for which (Art. 74) Violle found that the specific heat at any temperature τ between 0° C. and 800° C. may be represented by the expression $S_\tau = \cdot 0317 + \cdot 000012\tau$.

As the melting-point of platinum is very high, and its specific heat fairly constant, a mass of that substance is sometimes placed in a furnace and then transferred to a quantity of water in order that the heat it gives out may give an indication of the temperature of the furnace. (See Miscellaneous Examples, No. 1.)

On the other hand, Weber found that carbon, in the form of diamond, showed a remarkably rapid increase of specific heat with increase of temperature; and Dewar, by dropping a known weight of the substance into liquid air or liquid hydrogen and measuring the quantity of gas evolved, has shown its behaviour at low temperatures. Their combined results are—

Temperature ...	985° C.	606° C.	100° C.	−48° C. (mean)	−133° C. (mean)	−220° C. (mean)
Specific heat ...	·459	·441	·19	·0794	·019	·0043

The variation is thus seen to be very great, and not proportional to the temperature. The values obtained by these observers for graphite are nearly the same as those obtained for the diamond at high temperatures but considerably differeut at low temperatures, the range of variation heing again very large.

Many experiments have been made recently on specific heat at high and at low temperatures. The results given above are typical. The following values of the specific heat of ice may be noted—

Temperature	0° C.	−48° C.	−133° C.	−220° C.
Specific heat	·504	·463	·285	·146

Most *liquids* also show a large increase of specific heat with temperature. That of alcohol, as determined by Hirn, is at 160° C. greater than that of water, which at ordinary temperatures is greater than that of any other substance except hydrogen.

Battelli examined a considerable number of liquids between the

temperatures of $-20°$ C. and $-100°$ C., and found in all cases a diminution in the value of the specific heat as the temperature was lowered.

Water.—As the unit of heat is defined (Art. 67) as the quantity of heat necessary to raise unit mass of water through 1° C., it is a matter of importance to determine whether this quantity varies according to the point of the temperature scale at which the degree is selected.

In Regnault's investigations of the specific heat of water, made with the apparatus shown in fig. 40, he passed water at various temperatures above 100° into cool water. He seems to have satisfied himself that its specific heat was almost constant.

Jamin, employing the electrical method, found that the specific heat increases with rise of temperature, and at a rate greater than that assigned by Regnault.

Rowland, by an entirely different method, explained in Art. 214, found that as the temperature is raised from 4° C. the specific heat first diminishes and then increases, having a minimum value at 29° C., where it is about 1 per cent less than at 4° C. Rowland also made a series of independent experiments by mixing masses of water at different temperatures as Regnault did, and the results appeared to confirm those obtained from his previous method.

The elaborate series of experiments by Barnes place the minimum value at 37·5° C. (Art. 76).

Lüdin, in 1895, made some experiments by the method of mixtures, employing mercury thermometers. His results show a minimum value for the specific heat of water at about 25° C. and a maximum value at about 85° C. Griffiths, in the experiments described in Art. 218, found that it diminished as the temperature was raised from 15° to 25°. Bartoli and Stracciati employed the method of mixtures, immersing in the water contained in the calorimeter either cold water at 0° or warmer water, or a mass of metal whose specific heat was accurately known. They found that the specific heat had a minimum value about 20° C.

Thus the results obtained by Rowland have not been shaken by further investigation. A careful correction of his thermometers has led to slightly different values for the figures given in Art. 214, but the corrected figures still show a minimum value for the specific heat of water at about 30° C.

As to *gases*, Regnault's experiments made at various temperatures and pressures indicated that with air and the "permanent" gases, the specific heat remained constant. With carbonic acid, on the other hand, the specific heat was found to increase gradually with

An examination of the table shows that the law of Dulong and Petit holds good approximately within the limits of temperature of Regnault's observations; carbon, boron, and silicon, however, standing out as decided exceptions. Weber showed that the specific heat of these substances increased rapidly with the temperature up to a certain value, which then became approximately constant. If this value (shown in brackets in the table) be adopted, their atomic heats come out about 5·5. The recent work on specific heats at high and low temperatures has not yet disclosed any single set of conditions under which the law is exactly true for all the elements. For metals of high atomic weight, such as lead and gold, the atomic heat is about 6 at all temperatures, while for metals of low atomic weight it varies from 3 or 4 at low temperatures to 8 or 9 at high temperatures. The connection between atomic weight and specific heat generally is of a more complicated character than that expressed in this law.

Specific heat is a complex quantity. It has been seen that it varies greatly with temperature; and it includes (*a*) the heat required to raise the temperature of the substance, (*b*) the heat absorbed by the substance in expanding, and (*c*) possibly part of the latent heat of fusion, seeing that solid bodies often begin to soften long before they reach their melting-points. The first of these effects corresponds to the "real specific heat"; but how much heat is absorbed in the production of the second and third of these effects is in most cases unknown. Where, as in the case of many metals, there are certain temperature limits within which the specific heat remains nearly constant, the atomic heat approaches very closely to the average value 6·4. And it is probable that the atomic heats of the *solid elements* in a corresponding state would indicate but slight divergence from this average value.

(*b*) **Liquids.**—The law of Dulong and Petit is quite inapplicable to liquids. For example, bromine in the liquid state has a higher specific heat than solid bromine, while its atomic weight is of course invariable.

(*c*) **Gases.**—For the elementary permanent gases we have—

	Specific Heats at Constant Pressure.	Atomic Weights.	Atomic Heats.
Hydrogen	3·409	1	3·41
Oxygen	·2175	16	3·48
Nitrogen	·2438	14	3·41

These atomic heats are sensibly equal to each other, but quite different from those of solid bodies.

81. MOLECULAR HEAT. **Compound Substances.**—The molecular heat of a substance is the heat capacity of one **gramme-molecule** of the substance, i.e. of a mass equal to the molecular weight expressed in grammes, or the product of its specific heat and molecular weight. Regnault found that bodies having similar chemical formulæ have approximately the same molecular heat. Kopp investigated the specific heat of many solid salts, and found that the atomic heats of the elements as calculated from the specific heats of their compounds coincided with the atomic heats of the elements in their free state.

Neumann, who investigated the specific heats of many compound bodies of similar structural types, propounded the law that *the molecular heat of a solid compound is equal to the sum of the atomic heats of its constituent elements.* This statement is also sometimes referred to as Kopp's law. To take an example. In iodide of lead (PbI_2) the molecule contains an atom of lead and two atoms of iodine, and the sum of the atomic heats taken from the table in Art. 80 is 20·2. The specific heat of the substance being ·0427 and its molecular weight 461, its molecular heat ($·0427 \times 461$) = 19·7 as compared with 20·2 above.

As examples of compound gases, selecting those which approximately obey Boyle's law, we have—

Gas.	Specific Heat.	Molecular Weight.	Molecular Heat.
CO	·245	28	6·86
HCl	·185	36·5	6·76
CO_2	·217	44	9·54
SO_2	·155	64	9·95

The figures indicate approximately that the atoms have the same capacity for heat whether combined with dissimilar atoms or not.

Tilden has recently tested Kopp's law by a long series of experiments, at various temperatures between − 180° C. and 500° C., on the specific heats of compounds of tellurium with silver and nickel. He found that, at any temperature within this range, the sum of the atomic heats of the elements was always very nearly equal to the molecular heat of the compound. Similar agreement has been found in a large number of cases.

82. EXAMPLES.

1. Into a calorimeter whose temperature is 15° are placed 34 grm. of water at a temperature of 50° C. The temperature of the two becomes 20°. What is the water-equivalent of the calorimeter?

The heat given out by the water in cooling from 50° to 20° is $34 \times 30 = 1020$ calories.

Since 1020 calories warm the calorimeter through 5 degrees, its water-equivalent is $1020 \div 5 = 204$ grm.

2. The weight of a copper calorimeter is 110 grm., and the specific heat of copper is ·095. 400 grm. of water at a temperature of 16° C. are put into the calorimeter, and then 60 grm. of a substance which has been heated to 98° C. are placed in the water, whose temperature is now found to be 21° C. Find the specific heat of the substance.

Let S = the specific heat of the substance; then

(1) Heat emitted by substance $= 60 \times (98 - 21) \times S$ calories.

(2) Heat absorbed—

$$\begin{aligned} (a)\ \text{By water} &= 400(21 - 16)\ \text{calories;} \\ (b)\ \text{By calorimeter} &= 110(21 - 16) \times \cdot095\ \text{calories;} \\ \text{whence } 60 \times 77 \times S &= 5 \times (400 + 10\cdot45); \\ \therefore 924\,S &= 410\cdot45; \\ \therefore S &= \cdot444. \end{aligned}$$

3. A ball of copper at 98° C. is put into a copper vessel containing 2 lb. of water at 15° C., and the temperature of the water, ball, and vessel after the experiment is 21° C.; the weight of the vessel is 1 lb., and the specific heat of copper is ·095. Find the weight of the copper ball.

Suppose the ball to weigh x lb.; then

(1) Heat given out by the ball is—

$$x \times \cdot095 \times (98 - 21) = 7\cdot315x \text{ pound-degrees.}$$

(2) Heat absorbed—

$$\begin{aligned} (a)\ \text{by water is } 2(21 - 15) &= 12 \text{ pound-degrees.} \\ (b)\ \text{by vessel is } 1 \times \cdot095 \times (21 - 15) &= \cdot57 \quad ,, \\ \text{Whence } 7\cdot315x &= 12 + \cdot57; \\ \therefore x &= 12\cdot57 \div 7\cdot315 = 1\cdot718 \text{ lb.} \end{aligned}$$

4. A mass of 200 grm. of copper whose specific heat is 0·095 is heated to 100° C., and placed in 100 grm. of alcohol at 8° C., contained in a copper calorimeter whose mass is 25 grm., and the temperature rises to 28·5° C. Find the specific heat of alcohol.

(1) Heat given out is that from 200 grm. of copper when its temperature falls from 100° C. to 28·5° C.

$$\begin{aligned} H &= 200 \times \cdot095 \times (100 - 28\cdot5) \\ &= 19 \times 71\cdot5 \\ &= 1358\cdot5 \text{ calories.} \end{aligned}$$

(2) Heat absorbed is divided into two parts—

(a) That absorbed by calorimeter weighing 25 grm. when its temperature rises from 8° to 28·5°.

$$\begin{aligned} h_1 &= 25 \times \cdot 095 \times 20\cdot 5 \\ &= 2\cdot 375 \times 20\cdot 5 \\ &= 48\cdot 7 \text{ calories.} \end{aligned}$$

(b) That absorbed by 100 grm. of alcohol of specific heat S when its temperature rises from 8° C. to 28·5° C.

$$\begin{aligned} h_2 &= 100 \times S \times 20\cdot 5 \\ &= 2050 \text{ S calories.} \\ \text{Now } H &= h_1 + h_2, \\ 1358\cdot 5 &= 48\cdot 7 + 2050 \text{ S}; \\ \therefore 2050 \text{ S} &= 1309\cdot 8, \\ S &= \cdot 639. \end{aligned}$$

QUESTIONS AND EXERCISES

1. One pound of iron at 50° is put into water at 0°; contrast the effect with that produced by adding one pound of water at 50°.
2. Describe the method and apparatus employed by Regnault to determine the specific heat of a metal.
3. Describe some method of measuring the specific heat of a liquid.
4. Explain how the specific heats of two substances may be compared by heating them and noting their rates of cooling. If you wished to compare in this way the specific heats of water and turpentine, state exactly how you would proceed.
5. Equal known quantities of oil and water are placed in two calorimeters, and a coil of wire of unknown resistance is inserted in each. Currents of electricity are passed through the wires, the currents being adjusted so that the rise of temperature is the same in each of the two calorimeters. Show how to determine hence the specific heat of the oil, and explain what further data are requisite to make the measurement exact.
6. Explain how the specific heat of air at a constant pressure has been determined.
7. If the heat evolved by 1 kg. of water in cooling down from 100° C. to 0° C. were employed in heating 10 kg. of mercury initially at −20° C., to what temperature would the mercury be raised?
8. A solid at a temperature of 100° C. weighing 45 grm. is dropped into 120 grm. of water at 15° C.; the temperature of the resulting mixture is 19·6° C. Find the specific heat of the solid. What further experimental data are necessary to give an accurate result?
9. The specific heat of tin is ·064 in the Centigrade scale. What is it in the Fahrenheit scale?
10. A mass of 150 grm. of platinum at 90° C. is placed in 100 grm. of turpentine contained within a copper calorimeter whose mass is 30 grm. and whose temperature is 15° C. The final temperature of the whole is 21·7° C. Find the specific heat of the liquid, if that of copper is ·095, and of platinum ·032.

11. What is meant by the specific heat of a substance? A copper calorimeter of specific heat 0·095 has a mass of 120 grm. and contains 280 grm. of water at 15° C. Find the specific heat of a substance when 375 grm. of it at a temperature of 100° C. will when immersed raise the temperature of the water to 25° C.
12. A ball of lead at 98° C. is put into an iron vessel containing 2 lb. of water at 15° C., and the temperature of the water, ball, and vessel after the experiment is 21° C., the weight of the vessel is 1 lb. Find the weight of the ball. (Specific heat of lead ·0314, and of iron ·114.)
13. A copper vessel having a mass of 64 grm. contains 300 grm. of water at 15° C. In this are placed 256 grm. of copper at 96° C., and the final temperature is 21° C. Find the specific heat of copper.
14. What is the relation between the specific heat of a compound and that of its constituents? What is meant by the phrase atomic heat?
15. Discuss the most prominent exceptions to the law of Dulong and Petit connecting the specific heat of a substance with its atomic weight.

CHAPTER VIII

LIQUEFACTION AND SOLIDIFICATION—LATENT HEAT

We have now to consider the processes of change of state, under what conditions those changes occur, and what quantities of heat are necessary to effect them.

83. LIQUEFACTION.—Most solids have been caused by heat to pass into the liquid state, although some substances melt only at very high temperatures, obtained by special means. Platinum and flint have been melted by placing them in a crucible of graphite in a furnace where a stream of air was maintained through very small pieces of coke, the combustion being thus very rapid, and giving the maximum temperature obtainable from burning carbon. Ruthenium, more refractory still, has been liquefied in the oxyhydrogen flame, and carbon itself by a combination of this with the electric arc. As our experimental resources have become more extensive, refractory substances have been successively reduced, and evidence is thus accumulating that all substances are capable of existence in each of these three states under certain particular conditions of temperature and pressure.

84. LAWS OF FUSION.—The laws of fusion may be conveniently demonstrated by placing small lumps of sulphur in a flask containing a thermometer, and applying heat. The mercury in the

thermometer gradually rises till it indicates about 115°, and remains stationary at that temperature till the whole of the sulphur is melted. When complete liquefaction has taken place, the temperature again rises. If the substance be then allowed to cool slowly, the temperature falls to 115°, and remains stationary till the whole mass has solidified, when it again regularly falls. The distinguishing feature of the process is the fact that although during the change of state heat may enter or leave the substance in large quantities, the temperature remains unchanged.

The temperature at which the melting takes place is different for different substances, and is affected to some extent by the pressure to which the substance is subjected (Art. 90).

When the pressure is that of the atmosphere, this temperature is called the **melting-point** of the solid.

We have thus a means of maintaining bodies at a variety of definite steady temperatures by keeping them in contact with some suitable substance which is in the process of melting.

If the above experiment be repeated with small lumps of sealing-wax or of glass, it will be found that the temperature never remains entirely stationary. The difference may be presented to the eye by a diagram such as fig. 44, where time is set off along the horizontal axis and temperature along the vertical axis.

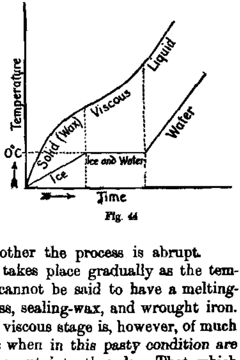

Fig. 44

Substances, then, may be divided into two classes according to their behaviour during liquefaction: in the one class the process is a gradual one, rise of temperature being accompanied by a gradual softening; in the other the process is abrupt.

When the process of melting takes place gradually as the temperature is raised, the substance cannot be said to have a melting-point. Such is the case with glass, sealing-wax, and wrought iron. The existence of this intermediate viscous stage is, however, of much practical use, since the substances when in this pasty condition are capable of being welded or drawn out into threads. That which follows here applies only to those substances in which this viscous stage, if it exist at all, is very short.

Latent Heat.—The heat that enters a substance during the process of liquefaction is said to be rendered **latent**. The word is a remnant of the language used at the period when heat was thought to be a subtle fluid, which in this process concealed itself from the thermometer.

The latent heat has not been destroyed, but has done work upon the particles of the substanee and communicated to them an equivalent amount of energy. (Art. 231.)

The latent heat of fusion of a substance is the number of units of heat required to change unit mass of the substance from the solid to the liquid state without change of temperature.

The **Laws of Fusion** then are—(i) Under ordinary atmospheric pressure each substance begins to melt at a certain temperature, which is constant for the same substance under the same pressure.

(ii) The temperature of the solid remains at this fixed point (called the melting-point) during the whole time of the process of change.

(iii) The melting-point of a substance depends on the pressure to which it is subjected; if the substance expand on solidifying, the melting-point is lowered by increase of pressure; if the substance contract on solidifying, its melting-point is raised by increase of pressure. (Arts. 90 and 298.)

(iv) Every suhstance during fusion absorbs heat. The quantity absorbed per unit mass is constant under the same conditions and is called the latent heat of fusion.

85. METHODS OF DETERMINING MELTING-POINTS.—The methods of determining melting-points vary very much according to the nature of the solid and the temperature at which it melts.

(i) For substances such as ice, the more easily fusible metals, and alloys which melt at ordinary temperatures and in which by stirring it is not difficult to maintain the whole mass at the same temperature, the following method may be employed. The substance is heated in a suitable vessel until a portion of it is liquefied. The temperature indicated by an immersed mercury thermometer when the mass is part liquid and part solid is the melting-point. It is sometimes convenient to place the thermometer in mercury contained in a copper vessel standing in the given liquid, rather than in the liquid itself.

(ii) For metals such as iron, whose melting-points are higher than the boiling-point of mercury, the temperature must be ascertained by one of the methods indicated in Chap. XVII.

Violle determined the melting-point of platinum in this way. He first found by the method given in Art. 74 that the true specific heat of platinum at any temperature within the limits 0° C. to 800° C. might be represented by the formula—

$$S_{\tau} = \cdot 0317 + \cdot 000012\tau;$$

and assuming that this formula held good up to the temperature of melting, he used it as a means of estimating that temperature thus: He melted a quantity of platinum and allowed it to cool slowly, so that a thin crust of solid began to form on the liquid. This crust he lifted off and placed in a calorimeter which contained a known mass of water at 0° C. The final temperature of the water was 15° C., and the number of units of heat given out by one gramme of platinum in cooling from x° C., its fusing-point, to 15° C. was found to be 74·7. But the total heat given out during the process of cooling is equal to the product of the mean specific heat (Art. 79) and the fall of temperature.

$$\therefore \ (\cdot 0317 + \cdot 000006x)\ (x - 15) = 74 \cdot 7$$
$$\therefore \ \cdot 000006x^2 + \cdot 03161x = 75 \cdot 16$$

a quadratic equation which gives $x = 1779$. (See Chap. XVII.)

(iii) For substances such as paraffin and wax, one may obtain a thin coating on the bulb of a thermometer by dipping it in the liquid substance. The thermometer may then be allowed to slowly cool, and its temperature read when the change of appearance that indicates solidification appears. The temperature should be then again slowly raised, and a reading taken when a change of appearance indicates that liquefaction has just taken place. The mean of these temperatures is approximately the melting-point.

Sometimes the substance experimented on is placed in a small tube and tied to a thermometer. Both being placed in a suitable water or oil bath, the changes of appearance and temperature are noted as before.

86. TABLE OF MELTING-POINTS.—The table given on p. 416 shows the chief results that have been obtained.

It may be observed that hard bodies have high melting-points; and that the values obtained for the melting-points of alloys are usually lower than those of the metals of which the alloys are composed.

87. METHODS OF DETERMINING LATENT HEAT.—The latent heat of any substance is usually determined by the method

of mixtures (Art. 70). Of substances ordinarily met with as liquids, the latent heat is determined by lowering the temperature of a known mass of the substance until it solidifies, placing the mass of solid in warm water, and noting the fall of temperature of the water as the substance liquefies.

Water.—The latent heat of water is the number of units of heat required to convert unit mass of ice at 0° C. into water at 0° C., and may be determined as follows:—

A quantity of water—m_1 grammes—at a temperature somewhat above that of the air is placed in a calorimeter whose water-equivalent is m_2 grammes, their common temperature being τ_1. Some small pieces of dry ice at 0° C. are then dropped into the calorimeter by means of a cold pair of crucible tongs, and the water is well stirred. When the temperature has ceased to fall, i.e. when all the ice is melted, the temperature τ_2 is taken. The calorimeter is again weighed, and its increase of weight gives the mass m_3 of the ice melted. Then if L be written for the latent heat of ice we have—

(i) Heat given out by the water and calorimeter in cooling from τ_1 to τ_2,

$$H = (m_1 + m_2)(\tau_1 - \tau_2).$$

(ii) Heat absorbed by the ice in melting $= m_3L$; and by the resulting water in rising from 0° to $\tau_2°$ in temperature a further quantity $= m_3\tau_2$, whence the total heat absorbed is

$$h = m_3(L + \tau_2);$$

wherefore finally

$$m_3(L + \tau_2) = (m_1 + m_2)(\tau_1 - \tau_2);$$

whence L is determined.

For example, if the calorimeter and contents were equivalent to 64 grm. of water which fell from 18° to 10° on the addition of 5·7 grm. of ice, we have—

$$\begin{aligned} 5{\cdot}7(L + 10) &= 64(18 - 10), \\ 5{\cdot}7\,L + 57 &= 512, \\ L &= 80 \text{ nearly}. \end{aligned}$$

It is best to avoid correction for radiation of heat from the calorimeter by arranging the experiment so that the final temperature of the water is as much below that of the air as its original temperature was above that of the air. This can be done by a preliminary trial and calculation from the approximate results thus obtained.

Person made use of ice below 0°, measuring the specific heat of ice simultaneously with its latent heat of fusion. His general arrangements have been described in Art. 70. Now, however, the ice was left immersed in the calorimeter until the temperature was uniform throughout, and the calculation was as follows, the initial temperature of the ice being of course below 0° C.:—

Latent heat of water = L.
Specific heat of ice = S.
Mass of ice at $-\tau_1°$ = m_1 grm.
Mass of warm water at $\tau_2°$ = m_2 grm.
Final temperature of the whole mass, τ_3.

Then we have—

(i) Heat absorbed by ice while its temperature was rising from $-\tau_1°$ C. to 0° C. .... = $Sm_1\tau_1$.
Heat absorbed by the ice in melting .... = Lm_1.
Heat absorbed by the cold water thus formed while its temperature was rising from 0° to the final temperature $\tau_3°$ ...... = $m_1\tau_3$.
(ii) Heat evolved by the warm water in cooling from $\tau_2°$ to $\tau_3°$ .... = $m_2(\tau_2 - \tau_3)$.
Whence $Sm_1\tau_1 + Lm_1 + m_1\tau_3 = m_2(\tau_2 - \tau_3)$.

Several experiments were made with different values for $-\tau_1$, and each pair gave two simultaneous equations to determine the two unknowns; or the value of S might be taken from the experiments given in Art. 72.

The value of L finally adopted by Person was 80·02; and from his experiments he was led to conclude that the process of liquefaction began at a temperature somewhat below 0° C., and that a portion of the latent heat of liquefaction (·75 unit) was taken in while the ice was below 0°.

The value obtained by Bunsen by means of his ice calorimeter (Art. 92) was 80, while Regnault's value was 79·25. A difficulty in Bunsen's method lies in determining the density of the ice. Bunsen's value for this was ·9167 at 0° C., while other observers make it as high as ·9176. If the latter value be taken, Bunsen's value for the latent heat of fusion of ice comes out 79·2. It is difficult *to eliminate bubbles of gas from ice as it is forming. Later* determinations of L appear to be in favour of a lower value than that of Bunsen.

A Metal.—Of substances which are ordinarily met with as solids

the latent heat is determined by raising the temperature of a known mass of the solid until it liquefies, placing the liquid in cold water, and noting the rise of temperature of the water. We give Violle's method for platinum. He allowed a certain weight of the molten platinum, which was in contact with its solid and therefore at melting-point, to run into a platinum eprouvette within a calorimeter, and found that the number of units of heat given out by 1 grm. of molten platinum in the double process of passing into a solid and then cooling to 15° C. was 101·7; and of this, as previously found (Art. 83), 74·7 units were given out during the cooling. Therefore 101·7 − 74·7 = 27 is the latent heat of platinum.

Glaser has made a number of determinations by the same method. His calorimeter was large, holding 40 litres. The metals were heated in an electric furnace (Art. 132) the chamber of which contained a gas that did not act chemically on the metal. He first found the specific heat of the metal at various temperatures, and from these values deduced its value at the melting-point. Thus knowing the specific heat at various temperatures, the heat given out by the solid in cooling could be more accurately calculated. The residual heat was, as above, due to the latent heat. His values were—for lead 4·78, zinc 29·86, aluminium 76·8, copper 41·6, and tin 13·6.

88. SOLIDIFICATION.—The process of solidification is the *converse of liquefaction. It usually takes place when the liquid* is exposed to a low temperature, but is with difficulty effected in the case of a few liquids. The study of this process involves the means of obtaining and measuring low temperatures.

Laws of Solidification.—(i) Under atmospheric pressure each substance begins to solidify at a certain temperature, which is always the same for the same substance under the same pressure.

(ii) The temperature of the liquid remains at this fixed point during the whole time occupied by the change. This fixed temperature, called the temperature of solidification, or in the case of water the freezing-point, is the same as the melting-point of the solid.

(iii) The temperature of solidification varies with the pressure (see Chap. XXVII).

(iv) Each substance during solidification gives out a quantity of heat equal to the heat rendered latent during fusion.

89. CHANGE OF VOLUME DURING SOLIDIFICATION. —It is a general rule that during the operation of melting expan-

sion takes place, so that the liquid is less dense than the solid at the same temperature. In Kopp's experiments on this subject the substance was enclosed in a thermometer tube, and covered with some suitable liquid. The change of volume was deduced from the change of level of the liquid in the tube. The following results were obtained:—

Substance.	Melting-point.	Volume at Melting-point.	
		(a) Solid.	(b) Liquid.
Phosphorus	44°	1·017	1·052
Sulphur	115°	1·096	1·150
Wax	64°	1·161	1·166
Stearic acid	70°	1·079	1·198

All these substances, as is usual, expand on melting.

In some cases, especially when solidification takes place slowly, the solid is deposited in the crystalline form, as in the case of bismuth; and when this occurs the peculiar molecular arrangement causes the solid to occupy more space than the liquid. Of such exceptional substances water is again the most remarkable. To determine the density of ice Bunsen placed in a bulb a known mass of ice at 0° C. and filled the bulb up with mercury to a marked point. The ice was then melted, and while the water was still at 0° C. more mercury was passed into the bulb to fill it up to the mark. The mass of this additional mercury was found, and its volume was then known. This was the amount by which the ice contracted on melting. The value deduced for the density of ice was ·9167. Nichols weighed ice in air and in oil of known density, and found the density of slowly frozen pond ice to be ·918 and of artificially prepared ice ·916. Vincent and Leduc obtained values practically the same. At − 185° C., Dewar found the value ·93. At temperatures near 0° C. water is probably not homogeneous but consists of a solution of ice in water. If ice were heavier than water, so that it sank on forming, lakes and seas would gradually solidify from the bottom upward.

Cast iron is another important exception. This substance expands as it passes from the liquid to the plastic state, the amount of expansion being as much as 6 per cent; on further cooling to the solid condition it contracts to about the same extent. The fact of its expansion renders it peculiarly suitable for casting into moulds.

Bismuth appears to expand in passing from the liquid to the

solid state by about 2·3 per cent; the specific gravity of the hot liquid is in fact greater than that of the cold solid.

This change of volume does not in all cases take place at the definite temperature known as the melting-point, but extends through a small range of temperature in the neighbourhood of that point.

90. EFFECT OF PRESSURE ON THE MELTING-POINT. —It was pointed out by Professor James Thomson on theoretical grounds that in the case of substances which change their volume in passing from the solid to the liquid state, a change in the pressure to which they are subjected must change their melting-points. He showed (see Chap. XXVII) that for

Substances that expand in melting	increase of pressure raises the melting-point; decrease of pressure lowers the melting-point.
Substances that contract in melting	increase of pressure lowers the melting-point; decrease of pressure raises the melting-point.

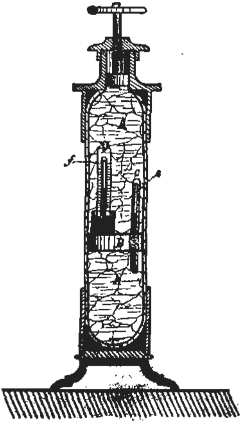

Fig. 45.

The change of pressure necessary to effect a large change in the melting-point is very great; the most extreme change that could occur in the freezing-point of water owing to change of pressure of the atmosphere would not exceed $\frac{1}{1500}$° C. Theory shows that water would freeze under a pressure of 2 atmospheres at a temperature of − ·0074° C. (see Art. 299).

Lord Kelvin experimentally verified the prediction thus made by means of the apparatus shown in fig. 45.

A mixture of water and lumps of ice, AA, was placed in a piezometer of thick glass, which also contained a manometer, *f*, and a thermometer, *e*. The manometer and thermometer were maintained in a convenient position by a ring of lead, B.

The thermometer liquid was

sulphuric ether, whose coefficient of expansion is large. The instrument was therefore very sensitive, each division on the scale corresponding to a temperature difference of ·0078° C.; it was protected from external pressure by being sealed up within a tube, C. The pressure was measured by the manometer, *f*, consisting of a straight glass tube containing air and standing in mercury. The pressure was applied by turning the screw at the top. The results were—

Pressure in Atmospheres.	Fall of Temperature.	
	Observed.	Calculated.
8·1	·059° C.	·059° C.
16·8	·129° C.	·123° C.

Mousson, employing a pressure estimated at 13,000 atmospheres, obtained by means of a screw forced into water contained in a steel cylinder, caused water to retain its liquid state when immersed in a freezing mixture at − 20° C.

For substances such as wax and sulphur, which expand on melting, Bunsen showed that the melting-points were raised by increase of pressure. Two strong glass tubes were drawn out at each end into the form shown in fig. 46. A piece of wax was placed at D; the remainder of the tube up to the point F contained mercury; and the portion FE, which was graduated, contained air. One of the tubes was left open at E, the other was closed. Both were fastened vertically to a board which was lowered into water of known temperature. The expansion of the mercury produced in the closed tube immense pressure, which was measured by the manometer FE. In the open tube the pressure was always 1 atmosphere, and the behaviour of the substance in the two tubes could by this arrangement be conveniently compared. The water was first heated until the substance at D melted. It was then allowed to cool, and the temperature and pressure noted at which solidification took place. These were the results—

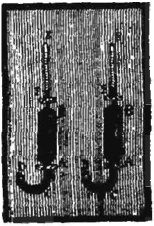

Fig. 46

Spermaceti.		Paraffin.	
Pressure.	Melting-point	Pressure.	Melting-point.
1 atmosphere	47·7° C.	1 atmosphere	46·3° C.
96 atmospheres	49·7° C.	85 atmospheres	48·9° C.
156 „	50·9° C.	100 „	49·9° C.

Hopkins extended these results to a pressure of 820 atmospheres, at which the melting-point of spermaceti was about 80°.

91. Glacier Motion: Regelation.—Forbes, in 1842, called attention to the motion of glaciers, which, although consisting of solid ice, flow along their beds in the same manner as a viscous fluid would do.

His explanation was of the following nature. Ice say at − ·1° C. is a hard solid, while at ·1° C. it has become a mobile fluid, and the change from perfect solid to perfect fluid does not take place suddenly and completely at 0° C., but is a gradual process extending through a small range of temperature about 0° C., just as iron, sealing-wax, &c., when their temperature is raised, gradually lose their distinctive solid properties and acquire more and more perfect fluidity. Forbes satisfied himself that the interior of a block of ice was both harder and colder than the outside, and as the temperature of a glacier is always close to 0° C. he concluded that a glacier is in a condition intermediate between that of ice and water, partaking of the hardness of the one and the fluidity of the other. But there is no evidence of the existence of this plastic condition in the case of ice.

Faraday pointed out in 1850 that two pieces of moist ice placed in contact will freeze together even in a warm atmosphere. This process—called **regelation**—is explicable on Forbes's hypothesis, because the colder ice on both sides of the thin film of water abstracts heat from the water and thus chills it to a temperature below that at which solidification commences.

Tyndall propounded the view that the ice of a glacier was continually being broken up by the forces to which it was subjected, and that the pieces afterwards froze together again; and showed that broken lumps of ice could be formed into one solid mass by pressing them together in a mould. The actual compression melts the surfaces in contact; the regelation takes place when the pressure is relieved.

The accepted explanation of regelation, however, is that propounded by Professor J. Thomson as derivable from the fact that the melting-point of ice is lowered by pressure. It has been shown (Art. 90) that under a pressure of 135 atmospheres water is solid below − 1° C. and liquid above that temperature, i.e. under this pressure ice at 0° cannot exist; it must melt. If two pieces of ice at 0° C. are in contact under this pressure melting must commence, and the absorption of heat that accompanies melting at once lowers the temperature. If, further, most of the water that has been formed escapes, carrying heat away with it, the temperature falls until the whole again freezes. And, generally, the application of stress to a mass of ice tends to melt it fastest at those parts where the stress is greatest and everywhere where there is any stress at all. The ice is thus in parts continually melting, only to re-form either wholly or partially in other parts.

In the case of Faraday's experiment the pressure between the parts was due to capillary action. The existence of such pressure is easily exemplified by the difficulty in pulling asunder two pieces of glass having a film of water between them.

The difficulty of making snowballs during a frost is due to the fact that the temperature of the snow is so far below 0° that the pressure applied is insufficient to melt it.

The following experiment was made by Bottomley. Over a block of ice supported at the ends he placed a wire, and hung weights on the ends of the wire. The wire gradually passed through the ice, but the block remained whole, because although the pressure under the wire caused the ice there to melt, the water thus formed escaped to the top of the wire and there froze again. When the ice melted under the pressure it absorbed heat, so that the water itself as well as the ice near it was thereby chilled to a temperature below 0° C. On escaping to the top of the wire the water was under only the ordinary atmospheric pressure and was below freezing-point, and therefore froze. Since the temperature of ice and water just beneath the wire is lower than that of the ice and water just above the wire, heat will therefore be conducted through the wire itself from its upper to its under side. The quicker this transfer takes place the quicker the cutting must proceed, because the water above the wire must part with heat in order to freeze, while the ice beneath the wire must receive heat in order to melt. This explains why it was found that with wires of different materials but otherwise alike the rate of cutting was roughly proportional to the conductivity.

92. ICE CALORIMETERS.—Since the melting of 1 grm. of ice is known to be effected by the absorption of 80 units of heat, we are able to find how much heat a body gives out in cooling, and therefore its mean specific heat, by observing how much ice it melts in cooling to 0°.

Fig 47

The form of calorimeter employed for this purpose by **Laplace and Lavoisier** is shown in fig. 47.

A large vessel C contains a smaller vessel B, and this a still smaller vessel A. The vessels B and C are filled with small pieces of ice at 0°. The body whose specific heat is to be determined is weighed, heated to a known temperature, and quickly placed in the vessel A. During its cooling it melts some of the ice in B, and the water formed is drawn off by a tap and weighed. The ice in the vessel C serves to ensure that no heat reaches B from the outside.

The value of the specific heat is calculated thus: Suppose 5 grm. of copper are taken from a chamber at 100° and placed in the receptacle A, and ·575 grm. of ice is melted, find the specific heat of copper.

Let S = specific heat required,

then (1) Heat evolved from copper = S × 5 × 100 calories.

(2) Heat absorbed by ice on melting = ·575 × 80 calories.

Hence 500 S = ·575 × 80;

∴ S = ·092.

This calorimeter is not adapted to give accurate results, because some of the water produced in B remains adhering to the ice. This difficulty has been avoided in the instrument next described.

Bunsen's Calorimeter.—Instead of determining the weight of ice melted, Bunsen suggested the measurement of the diminution of volume which takes place when ice melts. His calorimeter is shown in fig. 48. A reservoir AA′ contains in its upper part ice, and in its lower part mercury, which also fills the tube B and occupies part of the graduated capillary tube C. Into the vessel A is sealed

a test tube D, which contains a small quantity of liquid into which the substance whose specific heat is to be determined is dropped. As the substance in D cools to 0° C., the heat evolved melts some of the ice in A, and the resulting contraction in volume is indicated by the retreat of the mercury surface in C.

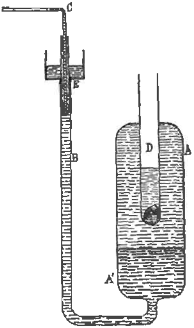

Fig. 48

It is necessary that there be no air within the vessel AA′, and for that reason the water and mercury are carefully boiled before being placed in that vessel. The process of filling is that described in Art. 7.

When the instrument is to be used it is placed in a vessel containing snow or ice, and a current of air is passed through some alcohol or ether placed in D (Art. 116), with the result that some or all of the water in A freezes. The liquid in D is then replaced by water at 0°, and the tube C raised or lowered through the collar E until the mercury in C stands at a convenient level. A small piece of the solid is then dropped into D, and the movement of the mercury surface in C observed.

The value in calories of the divisions on the stem C can be readily obtained by placing in D, x grm. of water at τ° C., and observing how many divisions on the stem correspond to this known evolution of $x\tau$ calories of heat. This method has the advantage of not involving a knowledge of the latent heat of water.

Or regarding the density of ice as known we may proceed by calculation thus:—

1090 c.cm. of ice make 1000 c.cm. of water.

∴ A reduction in volume of 90 c.cm. corresponds to the evolution of 1000×80 calories.

∴ A reduction in volume of 1 c.mm. corresponds to the evolution of $\frac{8}{9}$ calorie, and v c.mm. to $\frac{8}{9}v$ calories.

If the diameter of the bore of the capillary tube be accurately known reduction of volume is easily found, and the above relation then gives the quantity of heat evolved. If this heat be given out by m grm. of a substance whose specific heat is S in falling from τ° C. to 0° C., then

$$m \times S \times \tau = \frac{8v}{9}.$$

The instrument is used for the determination of the specific heat of substances that can only be procured in small quantities. By

means of Bunsen's calorimeter, for instance, Weber determined the specific heat of carbon in the form of the diamond. But it is difficult to obtain accurate results by it. Bunsen himself, in two determinations of the specific heat of calcium, got values differing by two per cent. The motion of the mercury in the capillary tube is apt to be jerky, and the density of ice is not accurately known.

93. LIQUIDS BELOW THE TEMPERATURE OF SOLIDIFICATION.—Water may by special means be maintained in the liquid state at a temperature considerably below 0°. Fahrenheit did this by exposing to a low temperature water sealed up in a spherical vessel. Gay-Lussac maintained water at − 12° C. by placing it in a flask, covering the surface with oil, and keeping it quite motionless. Despretz found that water in capillary tubes might remain liquid at − 20° C. In all cases, however, sudden vibration or contact with air produced immediate and rapid solidification; absence of air from the body of the liquid is necessary in order that the phenomenon may occur at all. Other substances may be made to give a similar result. Thus, if phosphorus be placed in water in a test tube, and the tube put in a beaker of water which is gradually warmed, the phosphorus becomes liquid above 44° C., remaining, however, at the bottom of the tube because of its greater density. If the beaker be then left to gradually cool, the phosphorus may remain liquid till the temperature is 30° C., but the immersion of a lump of ordinary (not amorphous) phosphorus at once provokes solidification.

The presence of a nucleus of some kind seems the necessary condition that solidification may take place at the normal temperature. Solidification of a liquid chilled below its point of congelation always takes place if a particle of the solid be dropped in the liquid. When the liquid thus commences to solidify, the latent heat of fusion is evolved, and the temperature immediately rises to the normal temperature of fusion.

94. SOLUTION.—A large proportion of chemical salts are soluble to a greater or less degree in water, the amount of salt that can be taken up by the water generally increasing with rise of temperature. Thus 100 parts of water dissolve about 17 parts of potassium nitrate at 10° C., 32 parts at 25° C., and 78 parts at 50° C. Sodium chloride (common salt) is a remarkable exception in this respect, 100 parts of water dissolving about 37 of the salt at any temperature between 0° and 100° C. For each salt a **solubility curve**

may be made showing how many parts dissolve in 100 parts of water at various temperatures.

The solution of the salt is itself accompanied by thermal changes. Thus if a measured quantity of water be placed in a beaker and quantities of common salt be gradually added to it, the temperature of the contents of the beaker is found to fall with each addition of the salt.

If sodium acetate be the salt used, the temperature of the solution is found to rise.

The **heat of solution** of a substance is the quantity of heat evolved or absorbed when unit mass of the substance is dissolved in a large *mass of water; and* **the molecular heat of solution** *is the heat of* solution of one gramme-molecule (Art. 81) of the substance. If m_1 grammes of water at temperature τ_1° be placed in a calorimeter whose water-equivalent is m_2 grammes, and m_3 grammes of a salt be added, the resultant temperature being τ_2° C.; then the quantity of heat absorbed or evolved is

$$H = \{(m_1 + m_3) S + m_2\} \{\tau_2 - \tau_1\}$$

where S is the specific heat of the solution; and the heat of solution is

$$\frac{1}{m_3} \{(m_1 + m_3) S + m_2\} \{\tau_2 - \tau_1\}$$

The molecular heat of solution is obtained from this expression by multiplying by the molecular weight of the salt. This quantity may be positive or negative.

All the more common gases dissolve in water with evolution of heat; most liquids do the same; solids more often with absorption of heat.

Depression of the Freezing-point.—*It is a matter of common knowledge that the freezing-point of sea water is lower than that of* fresh water. Sea water freezes at about − 4° C. Within limits the depression of the freezing-point of a solution of common salt in water is proportional to the strength of the solution.

Raoult's investigations showed that the freezing-point of any liquid in which a solid has been dissolved is lower than that of the pure liquid. The amount of this depression may be found by Beckmann's apparatus (fig. 49). The vessel for containing the solvent liquid is a long test tube A having near the top a side arm D. By means of a cork ring the lower part of A is supported within a larger

tube C, and this passes through and is supported by the lid of a large glass vessel E, which contains a cooling mixture adjusted to give a temperature two or three degrees below the freezing-point to be determined. The solvent liquid is poured into A, a thermometer T is inserted through the cork so that its bulb is in the liquid, and a stirrer F is also inserted. The stirrer F and a similar stirrer G placed in the cooling mixture are kept in motion, and the liquid in A, which is protected from rapid action by the air jacket in C, gradually cools to its freezing-point, which is read on the thermometer. The salt is then added through the tube D, and the new freezing-point determined in the same manner.

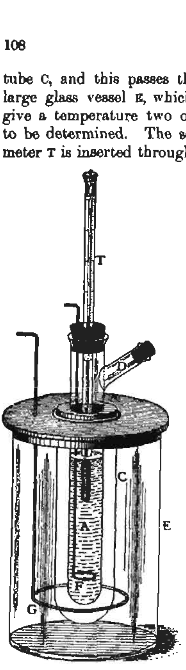

Fig. 40

Raoult's work proved that if there be dissolved in a large mass of a liquid solvent one gramme-molecule of a substance, then the lowering of the freezing-point is always the same whatever the substance dissolved may be, provided that the solution is dilute and non-electrolytic. The amount by which the freezing-point would be lowered when one gramme-molecule of a substance is dissolved in 100 grm. of a liquid is called the **molecular depression of the freezing-point.** For substances dissolved in water the value of the constant is about 18·5.

Thus if we dissolve 342 grm. of cane sugar in 10 litres of water, the freezing-point of the solution is depressed a certain number of degrees below that of pure water. The same depression of the freezing-point is produced by dissolving 126 grm. of crystallized oxalic acid or 32 grm. of formic acid, the numbers 342, 126, and 32 being the respective molecular weights of the substances dissolved.

On van t' Hoff's theory, solution is considered as the entry of the molecules of one substance into the spaces separating the mole-

cules of the solvent. The dissolved substance is in a condition analogous to that of a gas, and obeys the gaseous laws. Heycock and Neville have found similar results when gold is dissolved in sodium.

95. FREEZING MIXTURES.—When *liquefaction* is effected not by supplying heat from an external source, but by the process of solution, the quantity of heat absorbed is in some cases sufficient to cause the temperature of the solution and of bodies adjacent to it from which the heat is abstracted, to fall far below 0°. Such solutions are called **freezing mixtures**, of which the following are in most common use:—

(i) Powdered sodium sulphate or ammonium nitrate, dissolved in water, may lower the temperature of the solution to −15° C.

(ii) An ordinary means of producing a low temperature is by mixing together snow or powdered ice and common salt. These substances—both solids—when mixed, produce a liquid, the temperature of which may fall to −22° C.

(iii) By mixing calcium chloride and snow in the ratio of 4 parts to 3, a liquid is produced whose temperature may fall as low as −51° C.

Cryohydrates.—Guthrie found that if a weak solution of brine be exposed to gradually falling temperatures, the following phenomena occur. At a certain temperature a thin film of pure ice is formed, but some of the liquid remains unfrozen. On further lowering the temperature, more ice is formed, but some liquid still remains, the solution becoming stronger. This process continues till the remaining liquid is saturated with salt, which always occurs at −22° C., *and the saturated liquid then obtained freezes into a homogeneous solid. This solid is called a* **cryohydrate**. The nearer the liquid is to the point of saturation when the cooling commences, the lower must the temperature be reduced before any ice at all is formed.

If a saturated solution of brine be subjected to a similar process, the solution gradually becomes slightly weaker owing to the deposition of crystals of cryohydrates, and at − 22° C. the whole freezes. No solution of water and common salt can exist in the liquid form at a temperature below − 22° C. This, then, is the lowest temperature that can be obtained by mixing snow and salt.

The same results follow when other salts, e.g. iodide of potassium and sulphate of soda, are dealt with. **When a solid separates out from a solution the freezing-point of the remaining liquid is lowered, and ultimately the residual liquid solidifies at a constant temperature.**

It has been thought that cryohydrates are definite chemical compounds since they melt and freeze as a whole at definite temperatures. But they are now usually regarded as mixtures of the two mutually saturated solutions. The temperature at which the solid separates is the point of intersection of the curve of solubility with the curve which connects the temperature of freezing with the concentration of the solution.

96. EXAMPLES.

(L for ice taken as 79·5.)

1. How much mercury at 20° C. would be required to melt 1 kg. of ice at 0° C., the specific heat of mercury being ·033?

Let x kg. be the weight required, the unit of heat being the major calorie (Art. 67); then

i. Heat emitted by mercury in cooling from 20° to 0° $= x \times 20 \times \cdot 033$ unit.

ii. Heat absorbed by ice in melting $= 79\cdot 5$ units;

$$\therefore x \times \cdot 66 = 79\cdot 5;$$

$$\therefore x = \frac{7950}{66} = 120 \text{ kg.}$$

2. 1 kg. of ice at 0° C. is placed in 5 kg. of water at 0° C., and 1 kg. of steam at 100° C. is passed into it. What will be the temperature of the water if no heat is lost by conduction or radiation?

Let the heat unit be the major calorie.

Let the final temperature be x° C.; then

(i) Heat *given out* by 1 kg. of steam at 100° in condensing to water at 100° = 537 units.

(ii) Heat *given out* by 1 kg. of water at 100° cooling to x° = $(100 - x)$ units.

(iii) Heat *absorbed* by 1 kg. of ice at 0° in becoming water at 0° = 79·5 units.

(iv) Heat *absorbed* by 6 kg. of water at 0° in rising to x° = $6x$.

$$\therefore 537 + 100 - x = 79\cdot 5 + 6x;$$

$$\therefore 7x = 557\cdot 5;$$

$$\therefore x = 79\cdot 6° \text{ C.}$$

3. The specific gravity of ice is ·917. 10 grm. of metal at 100° C. are immersed in a mixture of ice and water, and the volume of the mixture is found to be reduced by 125 c.mm. without change of temperature. Find the specific heat of the metal.

Let x be the specific heat required; then

(i) Heat given out by the metal $= 10 \times 100 \times x = 1000\,x$ calories.

(ii) Heat absorbed by the ice in melting.

To change 1 grm. of ice into 1 grm. of water requires 79·5 calories.

$\therefore$ To change $\frac{1000}{\cdot 917}$ c.mm. of ice into 1000 c.mm. of water requires 79·5 calories,

i.e. „ „ 1090·5 „ „ 1000 „ „ „ 79·5 „

Reduction of vol. $=$ *90·5 mm. corresponds to absorption of 79·5 calories.*

$\therefore$ " " $= 125$ " " " " $\dfrac{79{\cdot}5 \times 125}{90{\cdot}5}$ "

$$\text{Hence } 1000x = 79{\cdot}5 \times \frac{125}{90{\cdot}5};$$

$$\therefore x = {\cdot}1097.$$

QUESTIONS AND EXERCISES

1. Explain carefully the statement that the latent heat of fusion of ice is 79·5. What is the unit in terms of which the latent heat is measured?
2. 2 lb. of ice at 0° C. are put in 5 lb. of water at 10° C. How much ice will melt?
3. 1 lb. of ice at 0° C. is put into 10 lb. of water at 26·5° C. What is the final temperature?
4. A mixture of ice and water is reduced in volume by 1 c.cm. What weight of ice has been melted?
5. What would be the volume at 50° C. of the water obtained by melting 100 c.cm. of ice at 0° C.?

   [Mean coefficient of expansion of water between 0° and 50° = ·000236. Specific gravity of ice = ·9167.]
6. How many units of heat would cause a mixture of ice and water to contract by 50 c.mm., if 100 c.mm. of water at 0° C. become 109 c.mm. of ice on freezing?
7. State the laws of fusion. What is the effect of pressure in changing the temperature at which water freezes?
8. Define what is meant by the "latent heat" of water; and state exactly how you will proceed to measure it experimentally.
9. The latent heat of tin is 14·25 in the Centigrade scale. What is it in the Fahrenheit scale?
10. What weight of ice would lower the temperature of 30 lb. of water from 15° C. to 12° C.?

    The heat of fusion of ice may be taken as 79 Centigrade units.
11. 1 kg. of tin at 0° C. is placed in 20 kg. of water at 0° C., and 1 kg. of liquid sulphur at 115° C. is passed into it. What will be the temperature of the water if no heat is lost by conduction or radiation? (Specific heat of tin = ·0548.)
12. A pound of ice and a pound of common salt, both at the same temperature (a little below zero Centigrade), are mixed together. Explain the considerable fall of temperature which occurs.
13. A mass of iron weighing 400 lb., and whose temperature is 440° C. and specific heat ·114, is placed in a mixture of ice and water. How much ice will be melted if the latent heat of fusion of ice is 79·5 Centigrade units?
14. It is found that 31·6 grm. of copper at 100° C. will just melt 3·8 grm. of ice. If the latent heat of fusion of ice is 79, find the specific heat of copper.
15. Explain the method employed by Bunsen to determine the specific heat of a small quantity of a substance by the melting of ice, and describe the apparatus employed.
16. In a Bunsen's calorimeter if the section of the capillary tube is 1·5 sq. mm.,

and the mercury surface is displaced through 4 cm. when 5 grm. of a substance at 85° are introduced; find the specific heat of the substance.

17. If 100 c.cm. of water in freezing becomes 109 c.cm. of ice, and the introduction of 20 grm. of a substance at 100° C. into a Bunsen's calorimeter cause the end of the column of mercury to move through 74 mm. in a tube 1 sq. mm. in section; find the specific heat of the substance. The latent heat of water may be taken as 80 units.

CHAPTER IX

PROPERTIES OF VAPOURS

We have now to consider the change of state from liquid to gas. The conditions under which vaporization can occur and the properties of vapours will be discussed in this chapter, and the heat changes that accompany the change of state will be treated of in the next chapter.

97. FORMATION OF VAPOURS IN VACUO.—The term vapour is very generally applied to the gaseous state of substances that are usually met with in the solid or liquid state.

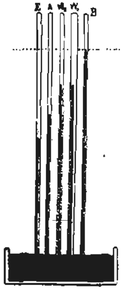

Fig. 50

Let several barometer tubes be filled with mercury and stand inverted in a mercury trough (fig. 50). The mercury will stand at the same height in all the tubes, and in the first tube, B, may remain unchanged throughout the experiment.

By means of a curved pipette introduce a very small drop of water into the second and third tubes, W_1 and W_2, which are of different sectional areas. In each tube the drop of water will, on reaching the vacuum, rapidly evaporate, and the column of mercury will fall. If water continue to be passed into these tubes in very small quantities the mercury for a time continues to fall, but before long a level is reached below which the mercury ceases to fall. Any further water that may be introduced ceases to evaporate, and forms a liquid layer on the top of the mercury. The height of the column is the same in W_2 and W_1.

Now let liquid alcohol be similarly passed up into tube A and ether into tube E. The result is of the same nature as before, but the amount of depression of the mercury column is different for each different liquid.

We have supposed that the temperature throughout has remained at some ordinary value, e.g. about 15° C. Let now the flame of a spirit lamp be cautiously brought near the thin liquid layers above the mercury in the tubes, and it will be found that some of the liquid will evaporate and the columns will be more depressed. If, on the other hand, any one of the tubes be cooled, some of the vapour condenses into liquid and the mercury rises.

The Laws of Vaporization in vacuo may be thus stated:—

(i) A small quantity of liquid introduced into a vacuum rapidly evaporates at any temperature.

(ii) The quantity of liquid that can be made to evaporate *in vacuo* at a fixed temperature is limited, and is proportional to the volume of the vacuous space.

(iii) The vapour thus formed exerts a pressure on the containing vessel. The pressure for any particular substance at any fixed temperature (under ordinary circumstances and not in capillary tubes) does not rise beyond a certain value, which is called the **maximum pressure** of the vapour at that temperature.

(iv) Vapours differ from each other in the value of the maximum pressure they can exert at any temperature.

(v) The maximum pressure varies with the temperature, growing greater as the temperature rises and less as it falls.

98. SATURATED AND UNSATURATED VAPOURS.—In the experiment just described the mercury continued at first to fall as more liquid was passed above it, but this fall ceased when a layer of liquid was formed above the mercury. Therefore in dealing with vapours in confined spaces an important distinction must be made. If liquid is present with its vapour, or, as it is commonly expressed, if the vapour is in contact with its liquid, that vapour is said to be **saturated**; it is exerting its maximum pressure, and is at its greatest possible density for that particular temperature.

If any additional pressure be put upon a saturated vapour it does not, as air does, increase in pressure as it diminishes in volume, but the vapour passes into the liquid state. If the pressure upon a saturated vapour be diminished, in order that the vapour may remain saturated, some liquid must evaporate.

Generally speaking, if a vapour is not in contact with its liquid

it is not saturated, although it is, of course, possible for saturated vapour to exist when not in contact with its liquid, as it does at the moment when on a slow rise of temperature the last particle of liquid evaporates.

If vapour be confined in a limited space with none of its liquid present, and in such quantity that it is exerting less than its maximum pressure, it is unsaturated. It can be converted into saturated vapour by sufficiently lowering its temperature or diminishing its volume.

99. UNSATURATED VAPOURS.—Unsaturated or superheated vapours approximate to the condition of the more permanent gases. We have now to determine whether they obey the gaseous laws—those of Boyle and *Charles*—and if so, under what conditions. The methods explained in Chap. V are not generally employed in dealing with vapours. The volume of a given mass of the vapour at different temperatures is not directly observed. The principle of the method usually adopted is to determine for each temperature and pressure the density of a given volume of the vapour as compared with air at the same temperature and pressure, taking care that no chemical action, such as decomposition into elementary gases, occurs to mask the purely physical laws.

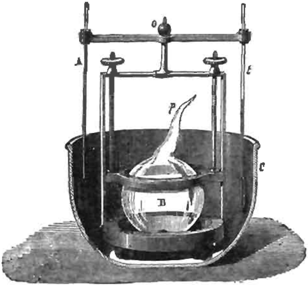

Fig. 51

As it is known that air obeys very approximately the laws of Boyle and Charles, the comparison serves to indicate the extent to which vapours obey them.

The density of a vapour at any temperature under the pressure of the atmosphere may be conveniently determined by the **method of Dumas**, whose apparatus is shown in fig. 51. A thin glass globe B has its volume and weight when full of dry air accurately determined. The volume of the globe being known, the weight of the

air within is calculated, and thus the weight of the globe itself is obtained.

In this globe B is placed a considerable quantity of the liquid whose vapour is to be examined.

The neck of the globe is then drawn out to a fine point *p*, and the globe is fixed in a bath C, which is heated to any required temperature, higher, of course, than the boiling-point of the confined liquid.

If the vapour investigated be steam, the bath may conveniently be of linseed oil, which does not boil until the temperature reaches about 375° C.

For the examination of vapours at a higher temperature baths of some fusible alloy or of zinc may be used.

The liquid within the globe is thus completely vaporized, and the aperture at *p* being sealed up, the globe is allowed to cool. It is then accurately weighed; and the weight of the globe itself being known, that of the vapour within is obtained. Also since the volume of the globe is known, the weight of the air which would fill it at the observed temperature is calculated.

The ratio between the weight of the vapour and that of the air at the same temperature gives the density of the vapour.

Victor Meyer's Method.—In this method the quantity actually measured is the volume of air displaced by the vapour evolved. The apparatus (shown in fig. 52) consists of a cylindrical bulb A, to which is attached a long thin tube B terminating in an enlargement C, and having just below C a side exit-tube D delivering over a pneumatic trough into a graduated vessel E. The bulb A can be heated in a bath contained in the vessel F.

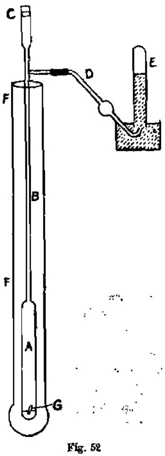

Fig. 52

A little asbestos having been placed in the bottom of A, the bulb is fixed in position in the bath F and heated to the temperature at which the determination is to be made, which must be well above the boiling-point of the liquid whose vapour density

is to be determined. The graduated vessel E being in position, the stopper C is momentarily removed, a small lightly-stoppered tube G containing a known mass of the liquid is dropped in on to the asbestos in A, and the stopper C is replaced. The contents of the tube G are expelled and vaporized at once, and the air displaced by the vapour thus formed passes along D and is collected and measured in E.

Let V be the number of cubic centimetres of air displaced at temperature τ and under barometric pressure P corrected for difference of level between the mercury surfaces and for the presence of aqueous vapour. Also let m = the number of grammes of liquid vaporized; then the corrected volume of the vapour formed is—

$$V \times \frac{P}{760} \times \frac{273}{273 + \tau},$$

and its density = mass ÷ volume is—

$$\frac{m}{V} \times \frac{760}{P} \times \frac{273 + \tau}{273} \text{ grm. per c.cm.}$$

To obtain the density with reference to air the above value must be divided by ·001293.

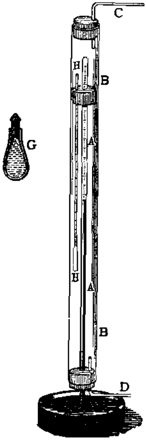

Fig. 53

Gay-Lussac's Method.—In this method the volume occupied by a known weight of the substance in the form of vapour at a known temperature and pressure is measured. The apparatus as modified by Hofmann is shown in fig. 53. A long graduated barometer tube A filled with mercury and standing in a mercury trough is surrounded by a larger tube B, into the ends of which are fitted smaller tubes CD. A stream of hot vapour from some suitable boiling liquid passes in at C through B and out at D, thus maintaining the barometer tube at the boiling-point of the selected liquid, which may be ascertained by the thermometer H. A known mass of the liquid whose vapour density is to be found is contained in a small stoppered bottle shown at G. When this is passed up the barometer tube the stopper is forced out, the liquid vaporizes and fills the space above the mercury. Thus the mass, volume, and

pressure of the vapour are all known, and the density is calculated from these data.

The following results have been obtained by Cahours for water vapour:—

Temperature (Centigrade)	107°	110°	120°	130°	150°	200°	250°
Density (air = unity) ...	·645	·640	·625	·621	·6198	·6192	·6182

If, as the temperature increased, water vapour expanded according to the same law as air, the density of the vapour relative to air at the same temperature as itself would be a constant quantity. An inspection of the above figures shows that this is not the case at temperatures near 100°, but that the approximation to constancy grows greater as the temperature rises. In other words, at temperatures not far above boiling-point unsaturated water vapour is more expansible than air at the same temperature; it does not obey Charles' law; but at higher temperatures it does so very nearly. There is no doubt but that at temperatures sufficiently high, water vapour would obey Charles' law as closely as air does.

By the same method Cahours also examined the vapour of acetic acid, and the variation of density with temperature was found to be of the same character as that of water vapour. At a temperature sufficiently above the boiling-point of the liquid, the coefficient of expansion of the vapour became sensibly the same as that of air.

Since, however, the boiling-point itself depends on the pressure (Art. 109), one mass of water vapour at 10° or 20° and at a low pressure, i.e. in a rarefied condition, may be as far removed from saturation as another mass at 200° or 300° under a higher pressure. Regnault, by a modification of his method for gases (Chap. V), examined the behaviour of unsaturated aqueous vapour *in vacuo* under feeble pressures at ordinary temperatures, and found that when the vapour was nearly saturated the gaseous laws were not obeyed, but that in proportion as it was further removed from the saturated condition the more completely did its behaviour approximate to that of air.

Several other methods have been employed which show the variations of density with pressure as well as temperature. Where the results are not complicated by the chemical phenomena of dissociation, or allotropic modification, the observations tend to the conclusion, which appears to have been placed beyond doubt by

Herwig's investigations, that each vapour, when very far removed from the saturated condition, has a definite density independent of the temperature at which it is observed. It is thus established that vapours far removed from the saturated condition obey both the gaseous laws, and their behaviour is in these respects not to be distinguished from that of the gases commonly called permanent. In Chaps. V and XI it is shown that the permanent gases obey neither of the gaseous laws when they are under such pressures and at such temperatures as to be near the point of liquefaction. There is, therefore, no fundamental distinction between gases and vapours; the differences observed in ordinary experiments are merely due to the fact that those experiments are carried on under such conditions of temperature and pressure that the "vapours" are nearly or quite saturated, while the "gases" are far removed from that condition.

100. VAPOUR DENSITY AND MOLECULAR WEIGHT. —The determination of vapour densities is of more especial interest to the chemist, and in reference to molecular theories. According to the law of Avogadro (Art. 233), equal volumes of gases or vapours under the same conditions contain the same number of molecules; hence a determination of the relative densities of gases and vapours is a determination of the relative weights of their molecules. The real density of a gas or vapour is the limiting value that is reached at temperatures far above the boiling-point.

The molecular weight of a substance which can be obtained in the gaseous condition is obtained by doubling its density as compared with the density of hydrogen.

Thus we have—

Gas.	Relative Density.	Molecular Weight.	Mass of one Gramme-molecule.	Weight of 1000 c cm.
			grammes.	grammes.
Hydrogen	1	2	2	·0896
Oxygen	16	32	32	1·4336
Nitrogen	14	28	28	1·2544
Carbon dioxide ...	22	44	44	1·9712
Chlorine	35·5	71	71	3·1808

One gramme-molecule (Art. 81) of any gas occupies 22230 c.cm. at standard pressure and temperature. This is the volume occupied *by 2 grm. of hydrogen, 32 of oxygen, &c. Many numerical results for individual gases become common when we deal with one gramme-*

molecule, because in this quantity there are the *same number of* molecules whatever the gas may be. Thus for one gramme-molecule of any gas (Art. 54),

$$R = \frac{PV}{\theta} = \frac{1{\cdot}0136 \times 10^6 \times 22330}{273}$$
$$= 82{\cdot}9 \times 10^6.$$

101. SATURATED VAPOURS.—If the vapour tubes of Art. 97 stand in a reservoir sufficiently deep, such as that shown in fig. 61, the pressure on the vapour may be increased by lowering the tubes in the mercury. If this be done slowly when the vapour is exerting its maximum pressure, it will be found that the height of the mercury column above the surface of that in the reservoir does not change. This shows that the pressure *of*, which is the same as the pressure *on*, the mercury does not change. The lowering of the tube is accompanied by a proportionate condensation of vapour into liquid. If a saturated vapour be compressed a portion liquefies, and if the changes of pressure and volume of the vapour take place slowly, so as to avoid disturbing effects, the pressure is constant and at its maximum value throughout. Whence it follows that Boyle's law is completely inapplicable to saturated vapours.

Fig. 54

102. VARIATION OF MAXIMUM PRESSURE WITH TEMPERATURE. — One of the most important investigations in this part of the subject is the relation between maximum pressure and the temperature.

To determine this relation Dalton employed the apparatus shown in fig. 54. The tube A was an ordinary barometer, the tube B was exactly similar, but had a few drops of water above the mercury.

Both stood in a mercury trough, and were surrounded by a cylinder containing water, which was slowly heated by a furnace below.

The difference between the heights of the mercury columns at any temperature showed the maximum pressure of the aqueous vapour at that temperature. When the water in the bath boiled, the mercury in B stood at the level of that in the cistern H, showing that when water boils the pressure of its vapour is equal to that of the atmosphere (Art. 109).

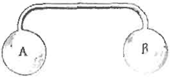

Fig. 55

Pressure in Communicating Vessels at Different Temperatures.—If two vessels A and B (fig. 55) in communication with each other, and containing nothing but water and water vapour, be maintained at different temperatures, the pressure in both tends to be that proper to the colder. The pressure in A, the warmer vessel, will be initially greater than that in B, the colder vessel, but the difference of pressure at once leads to a transfer of vapour to B, where it condenses, and thus diminishes the pressure to the value proper to the temperature of B.

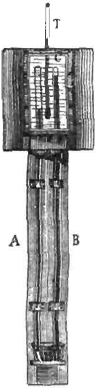

Fig. 56

Regnault's Experiments on Maximum Pressure of Aqueous Vapour.—The most accurate experiments on vapour pressure have been made by Regnault. He varied his method according to the temperatures employed.

(i) For temperatures between 0° C. and 50° C. the method was essentially that of Dalton, modified, however, in order to remove sources of error.

His apparatus is shown in fig. 56. Two barometer tubes A and B standing in mercury passed through the bottom of a metal box C having a plane front of plate glass. The box C could be filled with melting ice or with water of any temperature, which could be adjusted by a spirit lamp and read by a thermometer T. The tube B is an ordinary barometer, but A contains some water and water vapour above the mercury. The water in the vessel C was kept well stirred. The difference between the levels in the two tubes was read by a cathetometer, corrections being made for the layer

of water in A as well as for the difference in shape of the surfaces of the mercury in A and B.

Thus, for example, at the temperature 15° if there were 13 mm. difference of level and 4·25 mm. of water in A, the pressure of the aqueous vapour would be equivalent to that of $13 - \frac{4 \cdot 25}{13 \cdot 6} = 12 \cdot 69$ mm. of mercury.

(ii) For temperatures below 0° C. the apparatus was modified, taking the form shown in fig. 57. The vapour barometer A was bent round at the top and caused to end in a globe C. The water in C was at first contained within a small sealed bulb, and the bulb was broken by the application of heat. The water or ice within the globe was adjusted to the required temperature by surrounding it with a liquid freezing mixture of calcium chloride and snow. Different proportions of those substances gave different temperatures, which were read by a thermometer immersed in the mixture. By this means the pressure was observed at temperatures as low as − 30° C., at which temperature its value is only equivalent to that of ·01 in. of mercury.

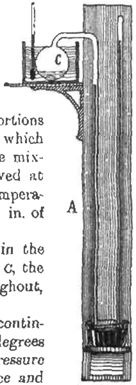

Fig. 57

Although the temperature of the vapour in the top of the tube A was not so low as that in C, the pressure, as shown above, is the same throughout, viz. that of the vapour in C.

Regnault's results showed no distinct discontinuity when the water became ice. For a few degrees below 0° C. he obtained the value of the pressure both when the vapour was in contact with ice and when in contact with water. The pressure of the saturated vapour in the presence of its solid was so nearly the same as in the presence of its liquid at the same temperature, that no difference could be safely inferred. Kirchhoff however, showed that such a difference existed.

(iii) For temperatures above 50° C., Regnault employed th apparatus shown in fig. 58. The method of obtaining the vapou at the different pressures was to cause the liquid to *boil* in an er closed space under an air-pressure which could be altered at will b a pump. The pressure of the vapour when the water boiled wa that of the air above it. The water was boiled in a copper vessel i

and the steam passed along a tube b into a reservoir C, which also communicated with one arm A of a Boyle's tube, of which the other arm B was about 80 ft. high and open to the atmosphere.

The tube e connected the reservoir C with the pump by which the pressure of the air in C was adjusted. Since this pressure was really the quantity to be measured it was necessary that it should not be liable to change from accidental changes of temperature. The globe C was therefore surrounded by a bath.

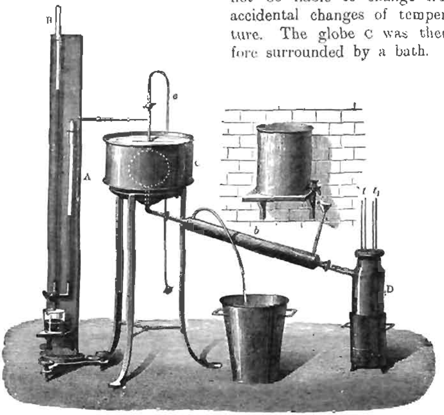

Fig. 58

The tube b sloped upwards, and was surrounded by a cold-water jacket, so that the vapour was there condensed and trickled back into the boiler D. The temperature of the vapour in D was read by delicate mercury thermometers t, t_1, the air thermometer being also employed.

Thus the vapour was produced and its temperature read in D; its pressure was adjusted by means of the air in C, and measured by the manometer AB.

An apparatus of this form, but stronger, was used to measure

pressures between 5 and 27 atmospheres, at which latter pressure the boiling-point of water is about 230° C.

The results of Regnault as corrected by Broch are indicated in as much detail as our space will allow in the table on page 417 and by the accompanying figure 59, in which curve II represents the variation of pressure with temperature between 0° and 100°, and curve I the variation between − 30° C. and 50° C., with the pressure changes set out on a scale ten times as great as in curve II.

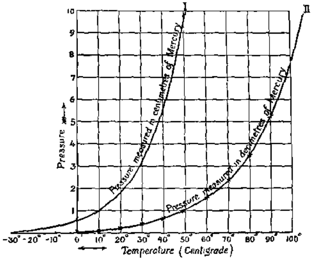

Fig. 59

Since the curves are *not straight lines*, the pressure does not vary in the same ratio as the temperature. Many attempts have been made to express the law connecting them by means of a formula.

The expression finally adopted by Regnault was the following:—

$$\log. P = a - b\alpha^x - c\beta^x,$$

where x is $\tau - 20$; P is the vapour pressure in millimetres, and $abc\alpha\beta$ are numerical constants.

The tables themselves are of great value.

By the same methods as those described above, Regnault determined the vapour pressure of alcohol, ether, and other substances. The only one that need be noticed here is mercury, the pressure of whose vapour he found to be ·746 mm. at 100° C. and ·02 mm. at 0° C. This pressure is practically insensible at all ordinary temperatures, and thus the reading of the barometer needs no correction on this account.

103. DENSITY OF SATURATED STEAM.—A knowledge of the behaviour of saturated steam being of great practical importance, Fairbairn and Tate investigated it by means of the apparatus shown in fig. 60.

Within a kind of thermometer tube A exhausted of air was placed a small known mass of water. This tube was placed in a reservoir B containing water, its stem being placed under the surface

of mercury contained in the bottom of the reservoir, which itself was immersed in an oil bath C standing in a sand bath D. The space above the water in B communicated with a manometer M, and contained a safety valve. As the apparatus was heated the water vapour in A was always at the same temperature as that in B, and at first the vapour in both A and B was saturated and exerting its maximum pressure. The pressures on the mercury surfaces at e were therefore equal, and the mercury stood at the same level inside and outside the stem. When, however, all the water in A was vaporized, water still remaining in B, further rise of temperature led to an increase of pressure in B over that in A, and a consequent rise of the mercury in the stem.

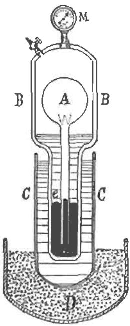

Fig. 60

At the instant when this rise commenced the known mass of saturated water vapour in A just filled a globe of known volume at the pressure and temperature given by the manometer and thermometer in B. The density of the vapour was thus calculable.

The temperatures at which determinations were made varied from 58° C. to 144° C., the quantity of liquid in A being varied in the different experiments, and the results were expressed by the formula

$$V = a + \frac{b}{P + c}$$

where V is the volume, P the pressure, $a = 25{\cdot}62$, $b = 1677{\cdot}6$, and $c = {\cdot}0244$. The tabular results are given on p. 417.

The results obtained by Fairbairn and Tate are not quite accurate, owing to the condensation which took place on the walls of the vessel A. They endeavoured to avoid this by first superheating the vapour 10° C. or 20° C. above the temperature of saturation, and taking the point at which condensation began as the mercury column was falling.

Perot made experiments on several vapours by the more direct method of weighing a bulb filled with saturated vapour at various temperatures. His values for steam are in general accord with those of Fairbairn and Tate, but are by no means identical.

The experiments demonstrate that the density of a saturated

vapour is greater than that calculated from the gaseous laws. But the specific volume of steam, i.e. the volume occupied by unit mass at any temperature, may be calculated with moderate accuracy from other data (Art. 300).

104. MIXTURE OF GAS AND VAPOUR.—Thus far we have spoken of single liquids evaporating *in vacuo*. Dalton examined the process when a liquid evaporated into a space already occupied by air, gas, or vapour by means of an apparatus similar to that shown in fig. 61. In that figure RR represents an iron reservoir terminating at the bottom in a vertical iron tube S, the whole containing mercury. In the bath stand three barometer tubes. Of these B serves as a standard barometer with which to compare the others, and the mercury in the tube V also originally stands at the same height as that in B with a vacuum above the mercury.

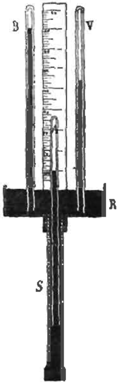

Fig. 61

Now let there be passed into the tube V a sufficient quantity of some volatile liquid to saturate the space; this will evaporate, exert pressure, and depress the mercury column through x millimetres, which is the measure of the pressure of the saturated vapour *in vacuo* at the temperature of the apparatus.

The tube A when placed in position contains some dry air. Its reading is therefore y millimetres below that of B, and the position of the mercury surface is marked on the tube. The same liquid as was used for the tube V is then passed into A in sufficient quantity to saturate the space above.

The total depression of the mercury column is now less than $x + y$ millimetres, because the air having expanded to fill the larger space exerts a pressure of less than y millimetres, its former value. To eliminate this effect the tube A is lowered into the reservoir until the surface of the mercury column stands again at the point marked; when this is done the air occupies the same volume as at first and therefore exerts the same pressure.

The total pressure of the gases in A is measured by the difference of level between the mercury surfaces in A and B, and this is found to be exactly $x + y$ millimetres, of which y millimetres is known to

be due to the confined air, and therefore x millimetres must be due to the vapour.

This value being the same as that for the vapour in the tube V, it appears that *the quantity of vapour which can exist in any limited space depends on the temperature only, and is the same whether that space be vacuous or already occupied by gas.* This is Dalton's law. It is assumed, of course, that the substances do not act chemically on each other.

The *rate* of evaporation is much greater *in vacuo* than when air or another gas is present.

If liquids be mixed, it is found that if the liquids dissolve each other the vapour pressure of the mixed liquid is less than the sum of the pressures of the constituents, but if the liquids are merely in juxtaposition without real intermixture the vapour pressure is equal to the sum of the pressures of the constituent vapours.

105. VAPOUR PRESSURE OF SOLUTIONS.—The vapour pressure of a liquid in which a salt has been dissolved is generally less than that of the solvent liquid, and the greater the proportion of the salt present the greater is the lowering of the vapour pressure. According to the theory of van 't Hoff, which is supported by Raoult's investigations, the relative lowering of the vapour pressure of a solvent on dissolving a non-volatile substance is equal to the quotient obtained by dividing the number of dissolved molecules (n) by the number of molecules (N) of the solvent; i.e.

$$\frac{P - P'}{P'} = \frac{n}{N}$$

where P is the vapour pressure of the pure solvent and P′ that of the solution. The lowering of pressure is independent of the nature of the molecules and is simply proportional to their number. The law is therefore generally applicable to all substances.

106. VAPOUR PRESSURE OF SOLIDS: TRIPLE POINT. —The pressure of aqueous vapour in the presence of ice is not quite the same as in the presence of water at the same temperature.

In fig. 62 the curve AB represents the relation between the pressure and temperature of water vapour in the presence of water when the temperature is near 0° C. This curve is called the **steam line**. The experiments described in Art. 90 show that the melting-point of ice is lowered by pressure. Hence if we have an enclosure filled with ice and water, no air and no vapour being present, the variation

of temperature with pressure will give a curve sloping in the direction CD. This is called the **ice line.** In an enclosure in which the temperature is never above 0° C., and in which ice and its vapour only co-exist, the variation of the vapour pressure with the temperature will trace out a line QE on the diagram. This is called the **hoar-frost line.**

Regnault's experiments did not justify the conclusion that the lines QE and QA were non-coincident. Kirchhoff, however, concluded that the two lines do not coincide; and Ramsay and Young found that when water and ice were contained in separate enclosures in contact with their vapour at the same pressure, the water was colder than the ice, indicating that QE and QA are separate curves. The three lines intersect at one point Q, which is therefore called the **triple point.** This point is obviously near to 0° C., as the three sets of conditions demand that ice, water, and steam shall exist together at the pressure and temperature indicated by Q. The temperature may be calculated thus: Since pressure lowers the melting-point of ice by ·0074° per atmosphere, the melting-point of ice under *no* pressure is ·0074° C. Now if ice be under the pressure of its own vapour, which is very nearly equal to that of 4·57 mm. of mercury or ·006 of an atmosphere, its temperature will be slightly lowered by this small pressure. The amount of the lowering is ·006 × ·0074° = ·0000444° C. The melting-point is thus ·0074° − ·0000444° = ·007356° C., which is the temperature of the triple point.

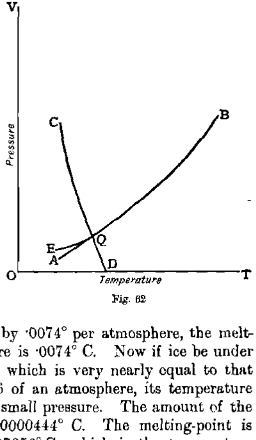

Fig. 62

107. DENSITY OF MOIST AIR.—It is often required to find the mass of water vapour present in a given volume of damp air. Proceeding on the assumption that the vapour obeys the gaseous laws, the expression may be obtained from that found for air in Art. 55 by multiplying that expression by ·62, which is the density of aqueous vapour compared with that of air. Thus we have—

Pressure in Millimetres of Mercury.	Temperature.	Mass in Grammes of one Litre (1000 c.cm.).
760	0° C. (273)	$\cdot 62 \times 1\cdot 293$
p	τ° C. = θ	$\cdot 62 \times 1\cdot 293 \times \frac{p}{760} \times \frac{273}{\theta}$

θ and 273 being the absolute temperatures corresponding to τ° C. and 0° C. respectively.

Then in a litre of moist air at the absolute temperature θ and at a total pressure P, the air containing vapour at a pressure p, we have—

(i) A litre of water vapour at a pressure p, weighing

$$\cdot 62 \times 1\cdot 293 \times \frac{p}{760} \times \frac{273}{\theta} = \cdot 4644 \times \cdot 62 \times \frac{p}{\theta} \text{ grm.}$$

(ii) A litre of dry air at a pressure P − p, weighing

$$1\cdot 293 \times \frac{P - p}{760} \times \frac{273}{\theta} = \cdot 4644 \times \frac{P - p}{\theta} \text{ grm.}$$

the combined mass being $1\cdot 293 \times \frac{P - \cdot 38p}{760} \times \frac{273}{\theta}$ grm.

When a gas is collected over water evaporation takes place at each bubble and the collected gas is generally saturated. The quantity of dry gas may be ascertained from the above expression.

108. EXAMPLES.

1. 100 c.cm. of oxygen saturated with water are collected at a pressure of 740 mm. and a temperature of 15° C. Find the volume of dry oxygen at 0° and 760 mm., having given that the maximum pressure of aqueous vapour at 15° is 12·7 mm.

If the aqueous vapour were removed there would remain 100 c.cm. of oxygen at 15° C. and (740 − 12·7) mm. pressure.

$$\frac{P_2V_2}{\theta_2} = \frac{P_1V_1}{\theta_1};$$

$$\therefore \frac{760}{273}V_2 = \frac{727\cdot 3 \times 100}{288};$$

$$\therefore V_2 = \frac{7273 \times 273}{288 \times 76}$$

$$= 90\cdot 7 \text{ c.cm.}$$

2. A quantity of dry air measures 4500 c.cm. at 10° C. and 760 mm. pressure. If the air be heated to 33° C. and saturated with vapour at that temperature, find the volume of the mass of air in order that the pressure may be doubled, the

elastic force of the vapour at 33° C. being represented by a column of 37·41 mm. of mercury.

(1) At 10°, $V_1 = 4500$; $P_1 = 760$; $\theta_1 = 283$.

(2) At 33° the total pressure is 1520, but of this 37·41 is due to the vapour. the pressure of the air is therefore 1520 − 37·41 = 1482·59,

$$\text{whence } P_2 = 1482{\cdot}59;\ \theta_2 = 306;\ \text{and } V_2 \text{ is to be found.}$$

$$\text{Since } \frac{V_1P_1}{\theta_1} = \frac{V_2P_2}{\theta_2}; \qquad \therefore V_2 = \frac{\theta_2}{\theta_1}\cdot\frac{P_1}{P_2}\cdot V_1.$$

$$V_2 = \frac{306 \times 760 \times 4500}{283 \times 1482{\cdot}59} = 2494 \text{ c.cm.}$$

QUESTIONS AND EXERCISES

(For Vapour Pressures see Table on p. 417.)

1. Define the terms *boiling-point of a liquid* and *saturated vapour*. State how the density of saturated steam at different temperatures has been measured.
2. State Dalton's law as to the pressure of a mixture of gases and vapours. By what experiments would you verify it for air and water vapour at a temperature of about 50°?
3. Give an account of the methods by which the maximum pressure of aqueous vapour at various temperatures has been determined.
4. 1 l. of dry hydrogen at 0° C. and 760 mm. pressure weighs ·08936 grm. Find the weight of 1 l. of hydrogen collected over water at 20° C. and 765 mm. pressure.
5. A quantity of air at 12° C. and 730 mm. pressure collected over water measures 250 c.cm. Find the volume of dry air at 0° C. and 700 mm. pressure.
6. Find the mass of 50 c.dm. of atmospheric air saturated with aqueous vapour at 27° C. and under a pressure of 740 mm. of mercury.
7. Find the mass of 6 l. of hydrogen collected over water at 18° C. and under 750 mm. pressure, given that 11·2 l. of dry hydrogen at 0° C. and 760 mm. weigh 1 grm.
8. 2000 c.cm. of oxygen at 15° C. and 753 mm. pressure has been collected over water. Find the volume of dry oxygen at 0° C. and 760 mm. pressure.

CHAPTER X

EBULLITION. LATENT HEAT

109. EBULLITION.—In the last chapter it was shown that a liquid under certain conditions passes into vapour at any temperature by the process of evaporation. At a certain temperature, however, this process gives way to boiling or ebullition, a mode of vaporization that for any fixed pressure takes place at one definite temperature only, when bubbles of gas are formed within the mass

of the liquid. The process of ebullition can be readily observed by boiling water in a flask over a spirit lamp. At first small bubbles are seen to form on the sides of the glass and to rise to the surface; these consist of air. Then at certain points of the heated lower surface larger bubbles are formed which diminish and collapse when they pass into the colder water above; these are steam. When these steam bubbles cease to collapse but reach the surface and pass into the space above, the water boils. If a thermometer be placed in the water it will continue to indicate a rise of temperature until this third stage is reached, when the mercury will remain stationary although heat continues to be absorbed by the liquid until the water has all boiled away.

If the process be repeated with alcohol, ether, sulphuric acid, and other liquids, it will be found that each liquid boils at a different temperature.

Effect of Pressure on the Boiling-point.—When we speak of the **boiling-point** of a liquid we mean the temperature at which the liquid boils under normal atmospheric pressure, for a liquid can be made to boil at temperatures considerably above or below that at which boiling usually takes place. In fact, by simply immersing the same thermometer on different days in boiling water, perceptible differences in temperature may be found, due to the ordinary variations in atmospheric pressure.

In an experiment devised by Franklin a flask is half-filled with water, and the water is made to boil for some time till most of the air has been expelled from the flask, which is then corked and inverted. If a lump of ice be then placed on the flask, ebullition recommences and continues until the temperature of the water is far below 100° C. This result is due to the condensation of the steam above the water, and the consequent diminution of the pressure on the surface.

The temperature at which any liquid boils under any given pressure may be determined by Regnault's apparatus, shown in fig. 58.

Any liquid boils at that temperature at which the pressure exerted by its vapour is equal to the pressure upon the surface of the liquid.

The boiling-point of any liquid under standard atmospheric pressure being thus a perfectly definite temperature, the immersion of a vessel in the vapour of a boiling liquid becomes one of the means of maintaining the vessel at a steady temperature. Thus the vapour of oil of turpentine gives a temperature of 159°, sulphuric acid 325°, mercury 358°, sulphur 444°, and chloride of zinc and cadmium still higher temperatures.

***Laws of Boiling*:—**

(i) At any fixed pressure each liquid begins to boil at a certain definite temperature. If the pressure be that of the normal atmosphere, the temperature of the vapour during ebullition is called **the boiling-point.**

(ii) During the process of boiling this temperature remains unchanged.

(iii) The temperature at which any liquid boils varies with the pressure.

(iv) During the process heat is absorbed or rendered latent.

The hypsometer.—The pressure of the atmosphere is less at the top of a mountain than at the sea level, and water therefore boils at a lower temperature on a mountain top.

By observing the temperature indicated by a thermometer immersed *in the steam* from water boiling under atmospheric pressure, we can, from Regnault's tables, deduce the pressure of the atmosphere, and when the pressure of the atmosphere is known the height above the level of the sea can be found. The instrument used, called a **hypsometer**, is shown and described in Art. 7.

The principle of the calculation is as follows: If we take a series of heights above the sea level which form an arithmetical progression, the heights of the barometric column at these stations form a decreasing geometric progression. From this it follows that the difference of level x between station A where the pressure is P_1 and station B where the pressure is P_2 is proportional to $\log_e \frac{P_1}{P_2}$, or employing ordinary logarithms

$$x = 2{\cdot}3\, Q\,(\log P_1 - \log P_2),$$

where Q is a constant. This quantity Q is the height of a homogeneous atmosphere, i.e. the height to which the atmosphere would extend if it were homogeneous, and everywhere at the same density as at the sea level. The value of Q is very nearly 800,000 cm. (about 5 miles). Hence

$$x = 1840000\,(\log P_1 - \log P_2).$$

Thus suppose at the hospice of St. Gothard water boils at 93°. Then reference to the tables of vapour pressure show that the pressure of the atmosphere is 58·8 cm.

If x represent the height above the sea level

$$\begin{aligned} x &= 1840000 (\log 76 - \log 58{\cdot}8) \\ &= 1840000 ({\cdot}1114) \\ &= 205000 \text{ cm.} \\ &= 6830 \text{ ft. approximately.} \end{aligned}$$

The process of finding heights by this means is called **hypsometry**.

Papin's digester (fig. 63) is employed for the purpose of raising water to a high temperature by heating it under great pressure. It consists of a very strong bronze vessel, the lid of which is held on by a screw. In this lid there is a valve, which is pressed down by a weighted lever, and from this valve steam escapes and lessens the pressure inside whenever that pressure becomes greater than that exerted by the weighted lever outside. The safety valve thus prevents the vessel from bursting. By a strong vessel of this kind water may be raised to a very high temperature; but the pressure is great, as much as 240 lb. on the square inch when the temperature is 200° C.

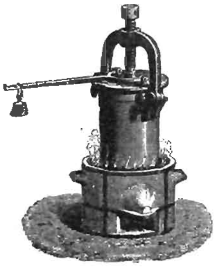

Fig. 63

The apparatus is used to effect operations which require water to be above 100°, such as the extraction of gelatine from bones. Some such contrivance must also be used to cook food in places where, owing to diminished pressure, water boiling in the atmosphere is not sufficiently hot to cook it.

110. RETARDATION OF BOILING.—The process of boiling has often some difficulty in commencing. This appears to be due to the absence of air. When water commences to boil the bubbles formed on the hot surface are small, and increase in size as they rise through the liquid. The origin of these bubbles is a small quantity of air present at their point of formation into which the water *evaporates*, and unless there be present within the liquid small bubbles of air into which this evaporation can take place, boiling does not commence at the temperature corresponding to the pressure. Thus pure water under the normal pressure boils at 100° C. in a metallic

vessel, but in a clean glass vessel its temperature may be raised several degrees higher before boiling commences.

Donny placed some water in a bent glass tube which had been most carefully cleaned, boiled the water for a long time to expel all air, and sealed the tube during ebullition. The water thus confined in a space almost perfectly destitute of air was raised to 137° C. without boiling, but at that temperature ebullition commenced with explosive violence.

Dufour prepared a mixture of linseed oil and essence of cloves, having a density equal to that of water at 100° C., and heated this liquid in an air bath. When the temperature was 120° a large drop of water was allowed to fall into the liquid. Part of the water passed into vapour, the remainder split up into small drops which, remaining suspended in the oil, retained the liquid state even when the temperature reached 180°.

When a liquid is in this **superheated** condition the introduction of the smallest quantity of gas or vapour produces violent ebullition. This effect follows the introduction of a solid rod, but it is almost certainly due to the air condensed on the surface of the rod. The gas need not be air, however, for the sudden ebullition takes place when a small quantity of any superheated liquid is decomposed by the passage of an electric current between two terminals immersed in the liquid, if one of the products of decomposition be a gas.

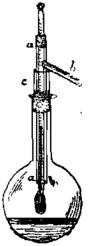

Fig. 64

111. DETERMINATION OF BOILING-POINTS. — This temperature may be conveniently determined by boiling the liquid in the hypsometer shown in fig. 3, or in a flask fitted up as shown in fig. 64. The vapour of the liquid passes up a tube *aa*, and issues by a tube *b*, whence it may, if necessary, be conducted to a cold vessel and condensed. The thermometer passes down the middle of the tube *aa*, so that its stem and bulb are all in the vapour and therefore at the same temperature, while an outer tube *c* protects from radiation that portion of *aa* which is outside the flask. The height of the barometer should be observed and a correction made for deviation from the standard pressure.

112. BOILING-POINTS OF SALT SOLUTIONS. — The general effect of dissolving a salt in a liquid is to raise the boiling-

point of the liquid, and up to the limit of saturation the more salt is dissolved the higher is the boiling-point. When the liquid is saturated the boiling-point is constant; the highest temperature obtainable with sea water under atmospheric pressure is 108° C.; with a solution of chloride of calcium a temperature of 120° C. may be attained. The steam given off from such solutions is pure water vapour, and at the instant of liberation, according to Regnault and Magnus, its temperature is that of the liquid. The temperature, however, rapidly falls, so that a thermometer placed a short distance above the liquid surface indicates the same temperature as if the vapour had been evolved from pure water. In Art. 105 it was shown that there is generally a lowering of the vapour pressure when a salt is dissolved in a liquid. Since a liquid boils at the temperature at which its vapour pressure is equal to that of the atmosphere, and the addition of salt reduces its vapour pressure below that value, the liquid must be further heated before boiling takes place.

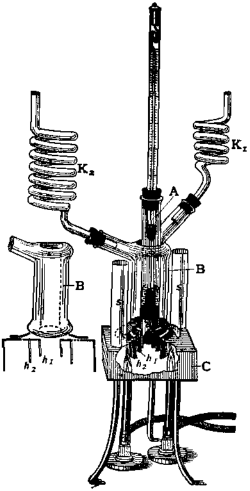

Fig. 65

The instruments for measuring temperature being more refined than those for measuring pressure, it is usual in this connection to measure the elevation of the boiling-point rather than the lowering of the vapour pressure. Beckmann's form of apparatus is shown in fig. 65.

The liquid is contained in a test tube A, which has a platinum wire inserted through the bottom and is filled to the height of a few centimetres with glass beads. Through the cork at the top is inserted a delicate thermometer. A side tube near the top allows

the salt to be added readily, and is connected with a condenser which returns the evaporated vapour into A. This tube A is surrounded by a jacketing tube B which contains a quantity of a suitable liquid, *either the same as that in A, or one that boils at a slightly higher temperature.* The jacketing tube is also at the top connected with a condenser. The stand is made in such a form that the heat supplied by the Bunsen burners underneath is applied to the jacket B and not to the boiling-tube A. To this end A is wrapped round with asbestos paper a, and rings $h_1 h_2$ of asbestos protect the bottom of it. The heating flames are placed outside these rings, and the hot gases are conveyed away by tubes S. *Thus the tube A is preserved from fluctuations of temperature.* The quantitative results are usually expressed in terms of the gramme-molecule (Art. 81).

The elevation of the boiling-point or the lowering of the vapour pressure produced by dissolving 1 gramme-molecule in 100 grm. of water is called the **molecular elevation of the boiling-point** or the **molecular lowering of the vapour pressure.**

Experiments show that—

(*a*) *The elevation of the boiling-point is proportional to the mass of salt dissolved.*

(*b*) The molecular elevation of the boiling-point is the same in amount for substances that are chemically similar.

Weak solutions in water of various substances of similar chemical composition are made, and the elevations of the boiling-point of these solutions experimentally obtained. Then the elevation that would be produced by 1 gramme-molecule in 100 grm. of water is calculated. *The results are all found to approximate towards the value* 5·2, provided that the solutions are non-electrolytic and non-volatile. As indicated in Art. 105, the elevation of the boiling-point is proportional to

$$\frac{\text{The number of molecules of the dissolved substance}}{\text{The total number of molecules in the solution}}.$$

113. *LATENT HEAT OF VAPORIZATION.*—When pure *water boils away into steam a large amount of heat is added to the system, but the steam is no hotter than the hot water. Every liquid* which does not change its composition during the process absorbs heat in passing into the gaseous state. This heat has ceased to exist; it has been transformed into molecular energy, which can, however, by suitable means be reconverted into heat. Conversely,

when a vapour is converted into a liquid, there is a conversion of molecular energy into heat and a rise of temperature (Art. 229).

The method of finding the latent heat of vaporization is to evaporate the liquid in a vessel, and then to allow the vapour to pass through a tube to a reservoir or spiral immersed in cold water, where it condenses into a liquid, and in so doing gives out its latent heat to the water with which it is surrounded, and whose rise in temperature allows the quantity to be determined. This is substantially the method of mixtures. In Despretz's apparatus, resembling fig. 40, and in that by which Andrews determined the latent heat of many vapours, the vessel in which the liquid was heated was a retort placed by the side of the calorimeter, with the neck sloping slightly upward. It requires a skilled experimenter to obtain anything approaching accurate results with this apparatus, owing to (1) the liability of liquid to pass into the calorimeter, (2) the superheating of the vapour, (3) conduction from the source of heat to the calorimeter. We therefore describe Berthelot's modification of this apparatus, by which he has obtained results as accurate as Regnault's, and which can be fitted up without much difficulty.

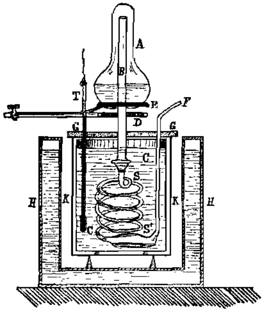

Fig. 66

The liquid is boiled in a flask A (fig. 66), which is closed at the top, and through the bottom of which passes a large vertical tube B. To this tube is fastened a spiral S, immersed in a calorimeter C containing water. The liquid in A is heated by a ring gas burner D, over which is placed wire gauze E, and as the tube BS is open to the atmosphere at F the liquid boils freely at atmospheric pressure. The calorimeter is carefully guarded from radiation from the burner by a series of screens, G, of wood covered with metal. A mass of the liquid is placed in A, and as the heating is continued vapour passes down the tube B and condenses in S′, the rise of temperature in C being given by the thermometer T. A small error arises

from conduction of heat along the glass of the tube B, which is corrected by observations of the thermometer T before and after the distillation process. The correction for radiation is made small and perfectly definite by surrounding the calorimeter with the water jacket H.

Then if m_1 = water-equivalent of calorimeter and contents,
m_2 = mass of vapour condensed,
τ_1 and τ_2 = initial and final temperatures of the calorimeter,
τ_0 = temperature at which the vapour condenses,
S = specific heat of the liquid,
and L = latent heat of the liquid,

we have—

(i) Heat given out

(a) By the vapour in condensing an amount $= m_2\text{L}$ units,

(b) By the condensed liquid in cooling from τ_0 to τ_2, an amount $= m_2(\tau_0 - \tau_2)\text{S}$.

(ii) Heat absorbed by the cold water and calorimeter $= m_1 (\tau_2 - \tau_1)$.

$$\therefore\ m_1(\tau_2 - \tau_1) = m_2\text{L} + m_2(\tau_0 - \tau_2)\text{S};$$

$$\therefore\ \text{L} = \frac{m_1(\tau_2 - \tau_1) - m_2(\tau_0 - \tau_2)\text{S}}{m_2}.$$

If the liquid be water the value of S is unity.

Thus suppose 1 oz. of steam at 100° C. to be passed into cold water at 15° C. within a calorimeter, the water-equivalent of the calorimeter and contents being 9 oz., and its initial and final temperatures respectively 15° C. and 77° C. Then if the unit of heat be that required to raise 1 oz. of water through 1° C. we have—

(i) Heat emitted (a) by steam in condensing = L units.

" " (b) by the water thus formed in cooling from 100° C. to 77° C. = 23 units. Total L + 23 units.

(ii) Heat absorbed by 9 oz. of water in being heated from 15° C. to 77° C. = 9(77 − 15) units.

$$\therefore\ \text{L} + 23 = 9 \times 62$$
$$\text{L} = 535.$$

This is approximately the value of the latent heat of steam at 100° C., and the method above described is suitable for the determination of the latent heat of vapours when boiling under atmo-

spheric pressure. But the temperature of boiling depends upon the pressure, and the value of the latent heat also varies with variation of the temperature of vaporization, i.e. with the pressure.

Regnault on Latent Heat of Steam. — The most important investigations on the latent heat of steam were made by Regnault. The essential parts of his apparatus are shown in fig. 67.

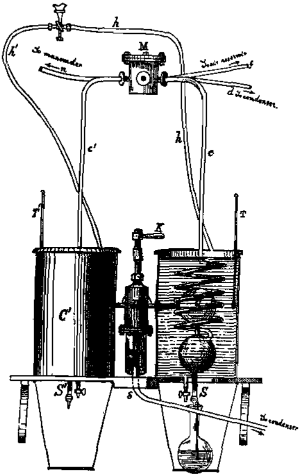

Fig. 67

The vapour was produced in a large vessel (not shown in the figure), inside which was a spiral through which the vapour passed, drying itself in the passage.

It then passed to *the regulator*, a cylinder R, from which tubes conducted it as required either to one of the calorimeters C, C′, or through δ to a condensing apparatus. In which one of these three directions the steam should pass was determined by the position of the handle K, which turned a piston that opened or closed the apertures in R.

The Calorimeters.—Two copper calorimeters C, C′ were employed, as exactly alike as they could be made, of the form shown in the figure. The water condensed during any experiment remained in the lower sphere, and was drawn off at S and weighed. The calorimeters were filled with cold water by means of the pipes h, h', which led from a small reservoir, whose capacity was accurately known.

The Pressure Arrangements.—As it was desired to measure the latent heat at various temperatures, it was necessary that the vapour should be subjected to various pressures (Art. 109). This was

effected in the following manner. A large reservoir of air, compressed or rarefied according to the pressure desired, communicated by a tube *f* with an enclosure M, from which there passed tubes *c*, *c'* to the lower spheres of the calorimeter, *d* to the condenser, *n* to a manometer, and another tube not shown in the figure to the boiler where the vapour was generated. Thus the vapour was everywhere at the same pressure as that in the air reservoir, and this was measured by the manometer, whence the temperature of the vapour was known (Art. 102).

Course of the Experiment.—The tap K was first placed so that the steam on entering R passed through δ to the condenser. This operation was continued for three-quarters of an hour, in order that the temperature of all parts of the apparatus might reach a stationary condition.

The calorimeters were then filled with water through *h*, *h'*, the steam turned into the globe C, and the rise of temperature of the thermometer T was observed. The operation was then repeated with the calorimeter C'. The object of having two similar calorimeters and using them alternately was that the corrections to be applied to the one in use might be obtained from the indications of the thermometer in the one that was not in use.

114. TOTAL HEAT OF STEAM.—It is shown above that the heat measured within the calorimeter is the result of two processes —the condensation of the steam and the cooling of the water thus formed. The total heat given out by unit mass of steam at τ° in condensing and cooling to 0°, or what is the same thing, the heat required to raise unit mass of water from 0° to τ°, and then to evaporate it at that temperature, Regnault called the **total heat of steam at τ°**. He determined this quantity for a wide range of temperatures, and found from his results that the value of this quantity H for 1 grm. of steam at any temperature τ might be expressed by the formula—

$$H_\tau = 606{\cdot}5 + {\cdot}305\,\tau.$$

Hence since the mere heating of the gramme of water from 0° to τ° C. takes τ units of heat, we have for the latent heat $606{\cdot}5 + {\cdot}305\,\tau - \tau$, or

$$L_\tau = 606{\cdot}5 - {\cdot}695\,\tau.$$

This expression shows that the latent heat decreases as the temperature increases.

Watt knew that the latent heat of water was less at 100° than at lower temperatures. *He had concluded that the difference was* equal to the difference between the sensible heats. This, however, is not the case. Regnault's formula gives—

$$\begin{aligned} \text{At } 0^\circ \text{ C., } L &= 606{\cdot}5 - 0 &&= 606{\cdot}5 \\ \text{At } 100^\circ \text{ C., } L &= 606{\cdot}5 - 69{\cdot}5 &&= 537 \\ \text{At } 872{\cdot}6^\circ \text{ C., } L &= 606{\cdot}5 - ({\cdot}695 \times 872{\cdot}6) &&= 0 \end{aligned}$$

The heat required to convert a gramme of water at 100° C. into steam at 100° C. is less by 69·5 calories than that required to convert a gramme of water at 0° C. into vapour at 0° C.

In explanation of this result, it may be pointed out that as the temperature of liquids is raised their molecular condition may approximate gradually to that of the gaseous state, and on this hypothesis a smaller expenditure of energy is necessary to complete the change of state at the higher temperature.

According to the calculation above, at the temperature 872°, there would be no difference between the liquid and gaseous states (Art. 121). Recent work indicates that the results of this article need revision. Thus experiments made to determine the critical temperature have given the value 365° C. instead of 872° C. Regnault's formula is not applicable to temperatures very different to those at which his experiments were made.

The rate of variation of the total heat, and therefore of the latent heat, with temperature, has been investigated by several physicists. Henning heated water by an electric current, calculated the heat supplied from the electrical data (Art. 133), and measured the quantity of steam produced. Between temperatures 30° C. and 100° C. his results were $L_\tau = 598{\cdot}8 - {\cdot}599\,\tau$. Smith passed dry air through water, thus causing evaporation, and kept the temperature of the water constant by passing an electric current round an immersed coil. Between 14° C. and 40° C. his results were $L_\tau = 597{\cdot}4 - {\cdot}58\tau$. Dieterici makes $L_\tau = 594{\cdot}8 - {\cdot}559\tau$, and Griffiths $L_\tau = 596{\cdot}7 - {\cdot}601\tau$ between 0° C. and 100° C.

The results of various observers are not very concordant in the value of the temperature coefficient, but there is reason to think that for temperatures below 100° C. Regnault's coefficient ·305 in the expression $H_\tau = 606{\cdot}5 + {\cdot}305\tau$ is too low, and that the simple linear law of that expression is only approximately correct.

115. COMPARISON OF LATENT HEATS.—The following method has been employed for the comparison of latent heats of

evaporation. The liquid is placed in a glass bulb which is enclosed in and communicates with a surrounding vapour jacket. Inside the bulb is a spiral of fine platinum wire ending in thick terminals fused through the glass. An electric current passed through the wire develops heat, and the vapour passes round the jacket. When the liquid has been boiling for some time and the whole has reached a steady temperature, then all the heat developed in the wire is spent in converting liquid into vapour and none in raising or maintaining the temperature. The energy supplied is capable of very exact determination (Art 133).

For comparison, two such bulbs containing different liquids are arranged in series, and the ratio of their losses in weight is inversely as their latent heats of evaporation.

Employing this method, Ramsay and Marshall obtained the following results:—

Substance.	Latent Heat, L.	Boiling-point, τ° C.	Molecular Weight, m.	Value of $m \times L \div \theta$.
Benzene	94·4	80·2	77·4	20·6
Toluene	86·8	110·8	91·3	20·6
Alcohol	216·5	78·2	45·6	28·1
Water	537	100	17·8	25·6
Methyl butyrate ...	79·7	102·7	101·2	21·4

Other liquids gave a result for column five of about 21. From many such observations Trouton has been led to formulate the law that *in liquids the molecular latent heat of vaporization* ($m \times L$) *divided by the absolute temperature of the boiling-point is a constant.*

The method indicated above has been applied to liquid oxygen, the liquid being contained in a vacuum vessel that stood in liquid air. The value of L obtained for oxygen was 58.

116. COLD PRODUCED BY EVAPORATION. FREEZING MACHINES.—When vaporization takes place without the presence of a flame or similar source of heat, the heat required to effect the change of state is abstracted from the liquid itself and from surrounding objects, which thus become colder. This is one of the methods by which low temperatures are obtained, rapid vaporization being produced by exposing a liquid surface in a vacuum.

Leslie devised the following experiment. He placed under the receiver of an air pump a small quantity of water in a shallow metal capsule over a dish containing concentrated sulphuric acid. On the

air being rapidly pumped out of the receiver the cold water commenced to boil quickly. The vapour produced was, however, absorbed by the sulphuric acid as fast as it was formed, and the heat required to produce the vapour being taken from the objects within the receiver their temperature fell, and the remaining water was frozen.

An elaboration of this apparatus by Carré forms a practical machine for freezing water. The water and sulphuric acid are placed in separate vessels communicating by a tube and connected with a special form of air pump. When the pump is worked the sulphuric acid is briskly agitated by a stirrer driven by a rod connected with the handle of the pump. The water vapour is absorbed as fast as it is formed, and evaporation takes place so rapidly that the water freezes almost immediately.

By evaporating liquids more volatile than water, more intense cold is produced. Thus, by surrounding mercury with sulphurous acid, and causing this volatile liquid to evaporate by passing a stream of air bubbles through it, sufficient cold is produced to freeze the mercury.

Carré's Ammonia Apparatus.—This apparatus consists of two iron vessels A and C (fig. 68) connected by a tube D. The vessel A

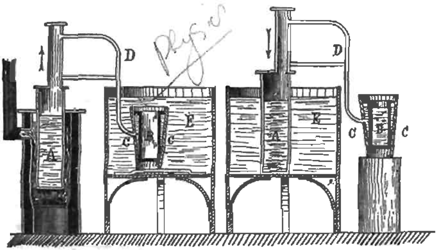

Fig. 68 Fig. 69

contains a strong aqueous solution of ammonia, and when this is heated the gas is driven off and condenses in the vessel C, which stands in a bath of cold water E, and contains within it the vessel B, enclosing the water to be frozen.

When the ammonia has been thus driven into C, the vessel A is removed to the cold-water bath E (fig. 69), and C is surrounded with some non-conducting substance. The liquid ammonia rapidly evaporates, passes along the tube D into the vessel A, where it is absorbed by the cold water. The heat rendered latent by the evaporation of the ammonia is obtained from the water in B, which is thus frozen.

117. SUBLIMATION.—Some solids, such as iodine, arsenic, camphor, ice, and carbonic acid in the form of powder, slowly evaporate without passing through the liquid state. The formation of hoar frost is a good instance of this process of sublimation. The water vapour does not liquefy and then freeze, but is deposited in the solid state. Flowers of sulphur are produced by the sublimation of sulphur vapour. For each solid there is a definite vapour pressure for every temperature. In many cases the pressure is too small to be measured. Just as each liquid has a boiling-point each snch solid has a subliming point, i.e. a fixed temperature at which, if heat be supplied to it, the substance passes into vapour whose pressure is equal to that of the atmosphere. Similarly it has a definite latent heat of sublimation, i.e. the quantity of heat absorbed in the vaporization of unit mass of the solid.

Ramsay and Young froze solid camphor round the bulb of a thermometer, and placed the thermometer in a vessel counected in one direction with an air pump and in another with a condenser kept cold by immersion in a freezing mixture. The pressure on the camphor was varied by means of the pump, and its temperature was read on the thermometer. At low pressures the camphor sublimed and its vapour passed into the condenser. At a pressure of about half an atmosphere the camphor liquefied. Under atmospheric pressure arsenic sublimes, but when heated in a closed vessel under higher pressure, melts. When the pressure of the vapour of a solid is not less than that of the atmosphere, the solid sublimes.

118. SPHEROIDAL STATE.—If a clean silver spoon be filled with water and held over a lamp, the temperature of the spoon does not become greater than the hand can bear, while any water remains in the spoon. If, however, the inside of the spoon be coated with some substance which water does not wet, the spoon becomes unbearably hot before the water boils.

When slightly moistened, one's hand may be thrust into molten iron without receiving injury. There must be, of course, lack of contact with the hot metal.

If a small quantity of water be dropped into a platinum or silver crucible kept at a red heat, the water does not pass into steam, but gathers itself into a spheroid, and remains for some time at a temperature below that of boiling. The liquid spheroid may often be observed to spin round on its axis as it slowly evaporates. If the heated metal consists of a smooth level plate, as shown in fig. 70, it can readily be seen that the globule of liquid does not touch the plate. This fact may be also proved by immersing in the liquid one terminal of an electric circuit, containing a battery and a galvanometer, and attaching the other terminal to the plate; no current passes, which proves that the circuit is broken.

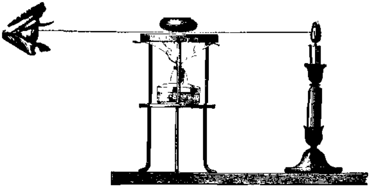

Fig. 70

This lack of contact between hot metal and adjacent liquid may be further exemplified by lowering a red-hot metal ball into water or into "Plateau's solution". In this experiment the ball may be seen to be surrounded by an envelope of vapour, within which it may remain red-hot for several seconds. When it has cooled to a temperature somewhat above the boiling-point of the liquid contact takes place, and vigorous ebullition begins.

Experiments have been made with many liquids with remarkable results. Boutigny poured liquid sulphurous acid into a white-hot platinum crucible; the liquid assumed the spheroidal state, and he then dropped water upon it. The water was quickly frozen, owing to the cold produced by the evaporation of the sulphurous acid. Using ether and carbonic acid, Faraday even froze mercury in this way.

The probable explanation of this peculiar condition of liquids is that owing to the layer of vapour that exists between the liquid and the hot metallic surface, the liquid receives heat only by radiation

or by conduction through the vapour. Recent researches point to the conclusion that most of the heat reaches the spheroid by conduction. The conducting power of gases and vapours is very small; hence the comparative coolness of the liquid spheroid.

119. EXAMPLES.

1. 10 lb. of water at 110° C. is suddenly exposed to normal atmospheric pressure. How much is immediately converted into steam?

When the exposure takes place the pressure is reduced, steam is formed, and the heat necessary to produce the change of state is abstracted from the mass of water, whose temperature rapidly falls.

Suppose the mass of steam formed to be x lb., then neglecting work done on the atmosphere,

$$\text{Heat absorbed} = 537x \text{ pound-degrees,}$$
$$\text{Heat given out} = 10 \times (110 - 100);$$
$$\therefore x = \tfrac{100}{537} = \cdot 186 \text{ lb.}$$

2. How many pounds of iron at 200° C. would be required to convert 10 lb. of ice at 0° C. into steam at 100° C.? Specific heat of iron = ·112.

Let x lb. be the mass required. The heat absorbed effects three operations:—

(1) Melting the ice requires	10 × 80	pound-degrees.
(2) Heating the water formed from 0° to 100° requires	10 × 100	„
(3) Evaporating the water requires	10 × 537	„
The total quantity is ...	7170	„

The heat given out by the iron in cooling from 200° to 100° is $100 \times \cdot 112 \times x$ pound-degrees.

$$\therefore 11 \cdot 2x = 7170.$$
$$x = 640 \cdot 2 \text{ lb. nearly.}$$

3. How much steam at 100° C. and 760 mm. pressure must be passed into 600 grm. of water at 0° C. in order to raise the temperature of the water to 100° C., supposing that 20 per cent of the heat is lost by radiation and otherwise?

Let the quantity be x grm.

Then the heat communicated to the water is $\frac{4}{5} \times 537 \times x$ calories.

The heat absorbed by the water in rising from 0° C. to 100° C. is 600 × 100 calories.

$$\therefore x \times \tfrac{4}{5} \times 537 = 60{,}000;$$
$$\therefore x = \frac{300{,}000}{2148} = 139 \cdot 7 \text{ grm. nearly.}$$

4. If the specific heat of a liquid be ·65, and the latent heat of evaporation constant and equal to 200 calories, find the total heat of the saturated vapour of the liquid reckoned from 0° C. at 0°, 50°, and 100° C.

$$\text{From Art. 114 } H_\tau = L_\tau + S \times \tau;$$
$$\therefore H_0 = 200 + 0 = 200,$$
$$H_{50} = 200 + 50(\cdot 65) = 232 \cdot 5,$$
$$H_{100} = 200 + 100(\cdot 65) = 265.$$

QUESTIONS AND EXERCISES

1. What is meant by *latent heat of vaporization*? If the latent heat of vaporization of water be 966 when 1° Fahrenheit is the unit of temperature, what will it be when 1° Centigrade is the unit? Would the result be different if the unit of mass had been changed?
2. Describe an experiment showing that water can be frozen by its own evaporation. What weight of vapour must evaporate in order to freeze a gramme of water already at freezing-point?
3. How would you determine the latent heat of ether vapour?
4. A jet of steam at 210° F. is passed into an open beaker containing a strong solution of a salt (say nitrate of soda) in water. The solution presently boils; its temperature is then tested by a thermometer, and found to be several degrees above the temperature of the steam which heated it. Account for this fact.
5. The latent heat of steam is stated to be 536. What does this mean? Describe in detail the experiments you would make in order to verify the statement.
6. Water is heated under pressure to 205° C.; on opening the valve of the apparatus steam escapes and the temperature falls to 100° C., when it is found that one-fifth of the water has escaped. From these data calculate the latent heat of steam.
7. 1 oz. of steam at 100° C. is passed into 9 oz. of water at 15° C., and the result is 10 oz. of water at 77° C. What is the latent heat of steam?
8. How much ice can be melted by 3·4 lb. of steam?

   [Latent heat of fusion of ice = 79·5 units Centigrade; latent heat of evaporation of water = 537.]
9. How is the boiling-point of water affected by external pressure? Explain what happens when water is placed in the receiver of an air pump where the pressure is not more than that of 3 mm. of mercury.
10. Find the temperature at which water boils on the top of Snowdon (3570 ft.), assuming 100° C. as the boiling-point at sea level.

    [Log 76 = 1·8808; log 66·3 = 1·8217.]

CHAPTER XI

LIQUEFACTION OF GASES

120. BOYLE'S LAW AT HIGH PRESSURES.—In Chap. V it was shown that Boyle's law was not rigidly obeyed by any actual gas, but that for pressures up to about 30 atmospheres the law might be regarded as a very approximate expression of the behaviour of the more permanent gases.

Cailletet and Amagat have extended these researches to pressures of 300 atmospheres. Cailletet employed a Boyle's tube of steel

having one arm about 800 ft. high, which was lowered down a deep artesian well, and into which mercury was poured. The short arm was coated inside with a thin layer of gold (which is dissolved by mercury), and the volume to which in any particular experiment the gas in the short arm was reduced was indicated by the length of that portion of the tube on which the gilding remained. The gas employed was nitrogen, and among the readings taken were the following:—

P In Metres of Mercury.	V	PV
39·36	207·9	8180
59·46	132·86	7900
79·23	103·0	8160
99·2	86·0	8536
182	51·3	9330

It will be noticed that the diminution in the value of PV as the pressure increases (Art. 44) does not continue beyond a certain point. When the pressure reaches that of 59 m. of mercury, the value of PV commences to increase.

Other gases were compared with nitrogen by means of Pouillet's apparatus (fig. 28).

Amagat made an extended series of experiments on nitrogen with apparatus similar to that shown in fig. 28, and then compared other gases with nitrogen by enclosing them successively in a manometer placed in a bath beside another manometer containing nitrogen.

The results of Cailletet and Amagat may be summed up as follows:—

(i) No gas accurately obeys Boyle's law.

(ii) The deviation from the law is different for each gas.

(iii) For all gases (except hydrogen) the compressibility is greater than that indicated by the law, until the pressure has increased up to a certain point; beyond that point the compressibility diminishes.

At this particular pressure the product PV has a minimum value, and the gas near that pressure obeys Boyle's law.

(iv) The value of the pressure for which PV is a minimum is different for each gas.

(v) In the case of hydrogen PV has no minimum value, but increases from the first.

Fig. 71, taken from vol. ix of the *Encyclopædia Britannica*, shows these results in a convenient manner, the excess or defect of the value of PV from the theoretical value given by Boyle's law being plotted against the pressure. If Boyle's law were accurately fol-

lowed the curve for each gas would be *simply the straight line* marked ·0. Starting from a pressure of about 25 atmospheres the hydrogen curve is practically a straight line, the value of PV steadily increasing. For other gases the value of PV at first *decreases and then increases* at an almost uniform rate. Ethylene and carbon dioxide gave curves of the same general character as that *shown for marsh gas, but* with a sharper inflection where the direction of the curve changes. The curves in the figure are drawn for one temperature only. At higher temperatures the curves for the more compressible gases become flatter. For very high pressures the curves become in all cases straight lines, for which the equation is $PV = Vb + Q$, where Q is a quantity dependent on the temperature, and b represents the least volume which the substance can occupy.

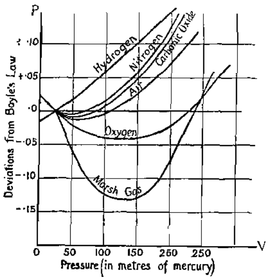

Fig. 71

121. THE CRITICAL STATE.—In some early experiments by Cagniard-Latour and Drion, peculiar effects were obtained, which have since been carefully investigated by Andrews and others. The substance was obtained in an intermediate condition, when it was neither liquid nor gas.

Fig. 72

Cagniard-Latour employed a curved tube, ABG (*fig.* 72), nearly full of mercury. He confined a liquid at A in a space very little larger than itself, and enclosed a quantity of air at G to serve as a manometer. The tube was placed in a suitable bath, and as the temperature rose the vapour of the liquid in A exerted a continually increasing pressure, which was registered by the compression of the air in G. When the temperature reached a certain value the surface of separation between the liquid and vapour in A ceased to exist; the whole became homogeneous. The pressure was very great, but at the somewhat high temperatures employed neither ether, alcohol, nor water could be retained in the liquid state.

By similar experiments Drion found that when the heating was very gradual the free surface between liquid and gas disappeared, and was replaced by a nebulous zone, which gradually increased upwards and downwards as the temperature was increased, until all became homogeneous.

A most important series of researches was made on this subject by Andrews. The substance chosen for experiment was carbonic acid, which is commonly met with in the form of a gas, but which can be liquefied by moderate pressure at a temperature easily attainable. His apparatus is shown in fig. 73.

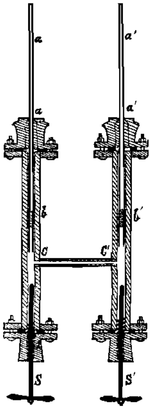

Fig. 73

The gas was contained in a strong capillary tube of glass *a*, the mouth of which was stopped by a pellet of mercury *b*. The tube was graduated so that the volume occupied by the gas at any time was immediately known, and was placed with its open end in water contained in a strong copper cylinder C. A quantity of air was similarly confined in a tube *a'* placed in a cylinder C', and the two cylinders were joined by a lateral tube, so that they were in hydrostatic connection, and the pressure was the same in each. This pressure was measured by the volume of the air enclosed in *a'*, and it was increased at pleasure by screwing in either of the screws S,S', which, exerting pressure on the water in C,C', forced up the pellets of mercury *b*,*b'*.

The temperature was regulated and maintained constant by surrounding each tube with a larger brass tube through which water circulated. Plate-glass windows in this brass tube allowed the capillary tubes to be seen.

So long as the temperature was below 31° C., Andrews found that as the pressure was increased the volume of the gas diminished, and when the pressure reached a certain value, liquid carbonic acid appeared in the tube. At 13·1° C. the pressure when liquefaction commenced was 47 atmospheres, at 21·5° it was 60 atmospheres, the pressure rising rapidly as the temperature was raised. When the temperature was above 31° C. it was found that by no increase of pressure that could be applied was it possible to produce the ordinary

phenomena of liquefaction in which liquid and gas exist together with a well-marked surface of separation between them. As the pressure was increased the volume diminished, but the substance remained homogeneous throughout in an intermediate state neither liquid nor gas.

Critical Constants.—Many investigations have since been made on gases and vapours, and it is found that they all exhibit the same phenomena in a greater or lesser degree. The behaviour of carbonic dioxide described above is typical, and indicates the general relation between the liquid and gaseous states. The temperature above which it is impossible to produce liquefaction of a gas by any pressure however great is called its **critical temperature**. For carbonic acid the temperature is 30·9° C.; for vapours, such as steam, it is very high; for the more permanent gases the critical temperature is very low, and it is therefore necessary to chill them strongly as well as to compress them in order to produce liquefaction. Air has been compressed at 15° C. by Cailletet until its density was nearly equal to that of water, without the definite change called liquefaction taking place.

When a substance is at its critical temperature there is a certain value of the pressure at which the substance is in a **critical state**, an unstable condition in which small changes of pressure and temperature produce a great effect on the substance. Thus, if the temperature and pressure be slightly below the critical values so that the substance is part liquid and part gas, a slight increase of temperature causes the surface between the liquid and gas to disappear.

The volume occupied by unit mass of the substance when in this state is called the **critical volume**, and the value of the pressure the **critical pressure**.

The following values have been obtained:—

Substance.	Critical Temperature.	Critical Pressure.	Critical Volume.
Carbon dioxide	30·9° C.	70 atmos.	·0066
Benzene	288·5° C.	48 „	3·29
Ether	193° C.	36 „	·013
Water	365° C.	200 „	·4

The values of the critical temperature and pressure are usually observed, and the critical volume then calculated from a knowledge of the densities of the liquid and the vapour, and the rates of change

of these densities with the temperature. To determine the critical temperature of water Cailletet enclosed water in a steel tube and heated it to various temperatures. At temperatures below the critical temperature the vapour pressure has a definite value for each temperature, but above that point the pressure varies also with the amount of water present. Using different quantities of water in different experiments, Cailletet determined the temperature at which this change of behaviour took place, and found the value 365° C., the pressure being 200 atmospheres. Galitizine made use of the fact that the refractive index of a substance in the liquid state is different from that of the same substance in the gaseous state, but the values approach each other as the critical temperature is approached. He found that for ether the values became identical at 193 C.

The direct determination of the critical volume is a difficult operation, because the rate of change of volume with temperature at the critical point is so great that the exact point is uncertain. Young heated the substances on which he experimented somewhat above the critical temperature, and then by a sudden expansion cooled them so that there was a separation between liquid and vapour. By gradually narrowing the limits within which this effect was produced, he determined approximately the critical volume of several substances.

122. LIQUEFACTION OF GASES.—*Gases such as sulphurous* acid, ammonia, and cyanogen, may be liquefied at ordinary pressures by simply lowering the temperature. This is done by causing the gas to pass from the apparatus in which it is produced into a vessel immersed in a freezing mixture, where it condenses into a liquid.

On the other hand, the application of pressure alone will cause many gases to liquefy at ordinary temperatures. Thus Pouillet, by the apparatus shown in fig. 28, liquefied at ordinary temperatures sulphurous acid, nitrous oxide, and carbonic acid gases by pressures of 2·5, 43, and 45 atmospheres respectively.

The liquefaction of the more permanent gases is only accomplished by subjecting them to great pressure at low temperatures.

The pressure required may be obtained either mechanically by forcing down a piston or screw so as to diminish the space within the vessel, or by causing the gas to be produced in large quantities in a small strong vessel, in which case the evolution of the gas itself produces the necessary pressure.

The low temperatures are produced either by freezing mixtures

or by surrounding the gas with a liquid which is made to evaporate rapidly. It is by the second of these means that the lowest temperatures have been obtained.

The method employed by Faraday for the liquefaction of chlorine and ammonia gas, was to place the materials by the chemical action of which the gas was produced in one end of a strong bent glass tube (fig. 74) and to immerse the other end of the tube in a freezing mixture. As the gas was evolved in the limited space, the pressure

Fig. 74

gradually increased until the liquid condensed in the cold end of the tube.

Thilorier's apparatus *for liquefying carbonic acid* is an elaboration of Faraday's bent tube; it consists of two cylinders of the form shown in fig. 75 connected by a strong copper tube. The cylinders are made of copper lined with lead, and bound round with strong bands of wrought iron. In one cylinder bicarbonate of soda and sulphuric acid are placed, the top is then screwed on, and the cylinder is rotated on a horizontal axis in order that the chemical ingredients may be thoroughly mixed. The gas is produced in large quantities, and the pressure rises to a value of from 50 to 80 atmospheres, under which the gas liquefies. The generating cylinder is

then by means of the strong copper tube placed in connection with the condensing cylinder, which is at a lower temperature, and the liquid distils over.

By relieving the pressure and thus allowing the liquid carbonic acid to evaporate rapidly, a portion of it is frozen, taking the form of white flakes closely resembling snow, which being a bad conductor of heat may be more easily preserved. In the presence of air the

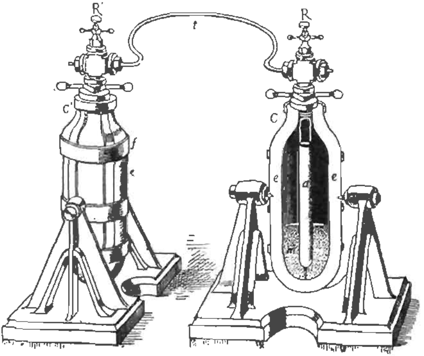

Fig. 75

solid slowly *evaporates at a temperature of* $-79°$. Solid carbonic acid formed into a paste by mixing it with ether, which serves the double purpose of rendering the substance a better conductor and of quickening the evaporation, forms one of the best refrigerating substances known. By immersing tubes containing liquid carbonic acid, nitrous oxide, and cyanogen in such a paste, and further hastening the process of evaporation by a pump, Faraday obtained those substances at about $-110°$ in the solid form, their appearance closely resembling ice. By the same method he succeeded in liquefying all known gases except six—viz., oxygen, nitrogen, hydrogen, oxide of carbon, dioxide of nitrogen, and marsh gas, which have been till lately called the "permanent" gases. All have since been liquefied.

Pictet's Experiments.—The principle of this method is that of Faraday's experiment. The apparatus employed by Pictet for the liquefaction of oxygen was of a complicated character; the general arrangements, however, may be understood from the accompanying diagram (fig. 76). Liquid sulphur dioxide was caused to pass into a cylinder AA′, where it evaporated rapidly under the influence of an exhausting pump also communicating with AA′. The result of this rapid evaporation was to produce a temperature of about $-65°$ C. within the cylinder AA′. Into a tube BB′ contained within AA′

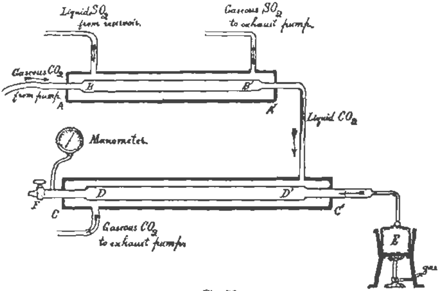

Fig. 76

gaseous carbon dioxide was forced by means of a pump, and when the pressure within this tube reached about 5 atmospheres (the temperature being $-65°$ C.), the carbon dioxide liquefied. The liquid carbon dioxide then passed through a tube into a long cylinder CC′ from which another tube passed to a second exhausting pump, which, causing rapid evaporation of the carbon dioxide, produced extreme cold (about $-130°$ C.) sufficient to solidify a portion of the carbonic acid. The oxygen produced in a very strong vessel E of wrought iron by heating potassium chlorate, passed into the condensation tube DD′ contained within the cylinder CC′. This tube was of steel about 4 m. long, had an internal diameter of 1 mm., was connected with a manometer, and terminated in a tap F.

On setting the pumps to work and applying heat to E, the pressure within DD′ continued to rise for about forty minutes, when

it became stationary, the manometer indicating a pressure of 500 atmospheres. The tap F was then opened, and oxygen issued from the tube as a white liquid which immediately evaporated.

Cailletet's Experiments.—The gas—as in Andrews' experiments on carbonic acid—was contained in a small glass tube, open at the bottom, with the mouth plunged in mercury.

The pressure was applied to the surface of the mercury by means of a powerful force pump, and arrangements were made so that by turning a tap the pressure could be instantly relieved. The upper part of the gas tube was surrounded by a cylinder containing cold water or a freezing mixture. Oxygen and carbonic oxide at a pressure of 500 atmospheres showed no trace of liquid when the temperature of the enclosure was 0° C., but on turning the tap and relieving the pressure the gas rapidly expanded, became chilled in the process, and a cloud was seen in the tube, which disappeared in a few seconds as the temperature again rose.

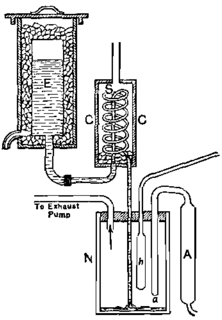

Fig. 77

Experiments of Wroblewski and Olszewski.—In these experiments the mode of compressing the gas was the same as that employed by Cailletet, but the extremely low temperatures employed gave results not before obtained. The gas tube A*a* (fig. 77) was bent round at the top, and the closed end *a* was contained within a vessel N, within which a very low temperature was produced and maintained in the following manner. A large quantity of liquid ethylene was placed in a cylinder E, and surrounded with a mixture of ice and salt at a temperature of $-17°$. The ethylene was allowed to flow through a tube into the vessel N, passing through a spiral S enclosed within a vessel C, which contained a mixture of solid carbonic acid and ether. The evaporation of this mixture produced a temperature of $-100°$ C. within the vessel C. When the liquid ethylene, thus reduced to $-100°$, reached N, it was continually exhausted by a pump. The rapid evaporation of the intensely cold liquid produced a temperature,

which, as registered by the hydrogen thermometer *h*, was $-136°$. At this temperature bisulphide of carbon, alcohol, and chloride of phosphorus, placed in N, were quickly solidified; and under a pressure of 20 atmospheres oxygen was obtained as a liquid in considerable quantities within the tube *a*.

Nitrogen and oxide of carbon were more difficult to liquefy than oxygen. At $-136°$ under 150 atmospheres pressure they remained gaseous, but were converted into liquid when the pressure was suddenly relieved, the lower temperature produced by the rapid expansion being below their critical temperatures.

Liquid oxygen being obtained with comparative facility, a quantity was procured and employed instead of ethylene as the refrigerating substance in further experiments, during which hydrogen, nitrogen, air, and carbonic oxide were liquefied and nitrogen solidified. Hydrogen proved the most refractory substance, remaining gaseous at a temperature of about $-200°$ (produced by evaporating liquid oxygen *in vacuo*) and under a pressure of 100 atmospheres. The production of a still lower temperature by means of rapid expansion, however, converted a portion of the gas into a liquid. The low temperature was estimated from the indications of a thermo-electric couple (Chap. XVII).

Dewar's Experiments.—In most of the above work the liquids were obtained in small quantities. Dewar has carried on work for many years at the Royal Institution, and has succeeded in obtaining large quantities of the liquids of most of the "permanent" gases; and retaining them in the liquid form at atmospheric pressure for long periods, has examined their properties.

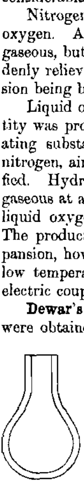

Fig. 78

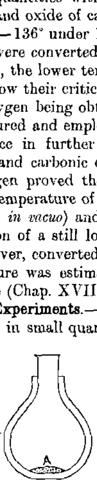

Fig. 79

The form of vessel invented by him for holding the liquids has double walls (fig. 78), the space between the walls being as perfect a vacuum as can be got with the inside faces silvered. Dewar finds that the effect of the high vacuum and the silvering is to reduce the heat that passes through the flask to the liquid to about one-thirtieth part of that which flows inward through the walls of an ordinary flask. He has also perfected the methods by making use of the absorptive power of charcoal. He found that this substance at the low temperatures employed shows an extraordinary power for absorbing gases, amounting to from thirty to

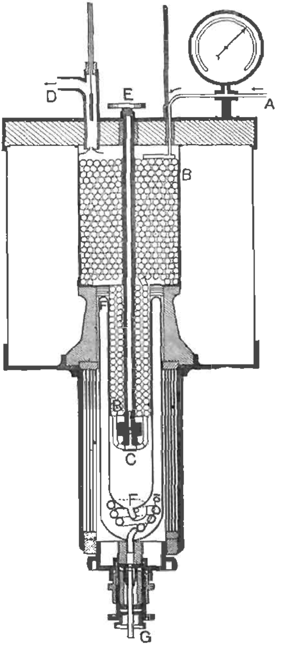

Fig. 80

seventy times as much at − 185° C. as at 0° C. Among other facilities that this affords is that the vacuum vessels can be made of metal, usually nickel or copper. A quantity of powdered *charcoal* is enclosed in a globular space A at the bottom of the flask (fig. 79), and by this means all gases passing through the metal walls are absorbed, and an almost perfect vacuum is maintained between the walls.

Self-intensive Method.—In the later methods of liquefying refractory gas the self-intensive method is employed, by which the *gas is cooled largely through* its own expansion. The experiments described in Art. 242 show that when air is forced under pressure through a small orifice it is cooled by ·26° C. per atmosphere of pressure. The same effect follows with other gases to a greater or less extent, hydrogen, which at ordinary temperatures shows a small heating effect, being at low temperatures also cooled by its own free expansion. The accompanying figure (80) shows the apparatus.

The gas—air, oxygen, &c.—enters the small pipe A at a high pressure—from 100 to 200 atmospheres—passes through a long coil

BB, emerges through a valve C, passes up through the interstices between the coils, and emerges into the atmosphere through the large pipe D. The valve C is controllable by the hand wheel E acting through a steel spindle. As the gas leaves C it expands under atmospheric pressure, and in so doing falls in temperature, and this cooler gas passing up on its way outside the coils to the aperture D, chills the coils. The gas on its way inside the coils towards the valve C arrives there colder in consequence, expands at C, and becomes colder still. And so the process goes on until the region round about C becomes so cold that drops of liquid form and fall into the vacuum vessel FF.

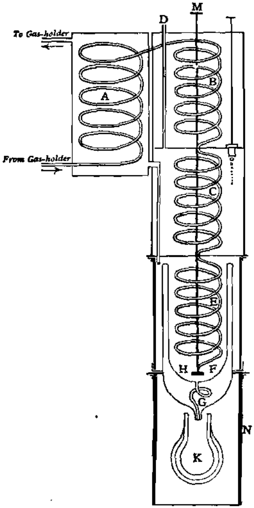

Fig. 81

This vessel (F) is made with double walls, the space between the walls being highly exhausted, and the interior walls themselves silvered, with the result that the heat passing from the exterior to the interior of F is greatly reduced. The collecting vessel is further protected from radiation by concentric glass cylinders with air between. The liquid that collects in F may be drawn off through the tube G, or the whole of the lower part of the apparatus may be detached.

The liquefaction of hydrogen is now effected on a commercial scale by similar means. Fig. 81 is a diagram of the apparatus. The gas is compressed in a suitable gasholder to about 150 or 200 atmospheres. It is then passed through a coiled tube A around which passes cold gas, and then through the coils in chamber B, which is filled with liquid air. Here the temperature is reduced to

about $-190°$ C. Some of the liquid air in B drops into the next chamber C, and on evaporating is exhausted by a pump through the pipe D. The hydrogen passing through a coil in C is thus further reduced in temperature to below $-200°$ C. It then passes into the regenerator coil E contained in a fourth chamber, and issues from a valve H which can be controlled by a spindle M. In passing through the valve to less than 1 atmosphere pressure the gas is cooled still further by its own free expansion. As this cold gas is pumped up through coils in the chambers E and C and through A it cools the whole apparatus still further, until after a few minutes, the temperature in F having fallen to about $-250°$ C., liquid hydrogen drops through the tube G into the vacuum flask K. When this flask is full, the chamber N can be detached and the flask removed.

123. SOLIDIFICATION OF GASES.—

Air.—Placing a litre of liquid air in a vacuum vessel, and subjecting it to rapid exhaustion, Dewar obtained about half a litre of solid air, which retained the solid state for a considerable period. At first it was a stiff transparent jelly, from which the still liquid oxygen was drawn out by placing the substance between the poles of a powerful magnet.

Nitrogen.—The solidification of nitrogen has also been effected by Dewar by passing through the liquid a stream of cold hydrogen gas, thus inducing rapid evaporation. The liquid nitrogen was contained in a vacuum vessel standing in another vacuum vessel containing liquid air. The hydrogen passed through coils inside these liquids, and was thus on its emergence into the liquid nitrogen at the same temperature as that liquid. Under these circumstances the nitrogen solidified in the form of long spiral tubes through which the hydrogen passed. The density of solid nitrogen was determined as 1·03.

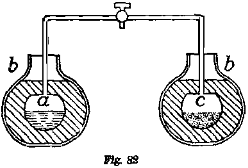

Fig. 83

Hydrogen.—Having obtained a quantity of liquid hydrogen in a vacuum vessel, Dewar connected the vessel to a pump, and by rapid exhaustion the liquid was caused to evaporate so quickly that it solidified, presenting the appearance of a froth of snow and bubbles. On immersing a tube containing liquid hydrogen in this foam, the liquid was converted

into a clear transparent solid. The temperature was estimated as 15° absolute.

Dewar has also obtained the refractory gases in the solid state by making use of the absorptive power of charcoal. Two bulbs (fig. 82), one, *a*, containing (say) liquid hydrogen and the other, *c*, powdered charcoal, were connected by a cross tube in which there was a tap. Each bulb was immersed in a vacuum vessel *b*, *b* containing liquid air evaporating slowly under atmospheric pressure. When the tap was opened the liquid hydrogen in *a* evaporated so rapidly that the liquid froze.

CHAPTER XII

HYGROMETRY

124. Since water exposed to the atmosphere is continually evaporating, and since the larger part of the earth's surface is covered with water, the air always contains water vapour in greater or less quantity, more in hot regions than in cold, less in inland districts than near the ocean; and this fact forms an important element of climate. The quantitative investigation of the state of the air as regards the moisture it contains is **Hygrometry**. The term **meteorology** is used in a wider sense; it is the science which deals with all circumstances affecting the weather.

125. EVAPORATION OF WATER INTO THE ATMOSPHERE.—The *rate* at which water evaporates when freely exposed to the atmosphere depends on the following circumstances:—

(i) The area of the exposed surface. Since evaporation is wholly a surface phenomenon, and takes place alike at every part of the surface, the mass of liquid evaporating per second is proportional to the area of the surface.

(ii) The dryness of the air. When the air is saturated no evaporation takes place, or, to speak more accurately, the rate of evaporation is equal to that of the condensation, which goes on simultaneously. When the air is perfectly dry, evaporation proceeds at its fastest rate.

(iii) The pressure of the air. We have seen that evaporation proceeds very fast *in vacuo* and much slower in the atmosphere. Dalton found that the rate was inversely proportional to the pressure on the liquid surface.

(iv) The presence or absence of wind. When wind is blowing over a small exposed surface of water the rate of evaporation is increased, because the air above the surface is then continually being replaced by air which is further removed from saturation.

(v) *For every liquid the rate also depends upon the nature of* the liquid, each having a special volatility.

126. CONDENSATION OF VAPOUR IN THE ATMOSPHERE.—The continuous evaporation of water is counterbalanced by its continuous condensation. This process may take place either on some cold surface, in which case dew or hoar-frost is deposited, or it may take place in the air itself, giving rise to fog, cloud, rain, hail, or snow.

Clouds.—A cloud is a collection of very small particles of water.

If a mass of air containing water vapour (which is invisible) be sufficiently chilled, the air becomes saturated, and if the temperature fall further, minute drops of water are produced, which in the aggregate form a cloud. This fall of temperature often occurs in the receiver of an air pump, and a cloud is formed during the process of exhaustion. So if a mass of warm vapour-laden air rise in the atmosphere it often becomes chilled below the point of saturation, with the same result.

Clouds, especially on mountain tops, are often stationary, but the particles that compose them are not so. The cloud may be compared to a busy city street, which from a distance looks about the same for several successive hours, although the individuals which make up the aggregate change from minute to minute. When the water drops are formed they commence to fall or to be blown away by the wind, but the space vacated is filled up by fresh vapour-laden air, whose vapour is in turn condensed.

The fall of these very small water drops in still air is exceedingly slow, *owing to the viscosity of the air.* This may be illustrated by observing the slow rate of falling of fine sand in water. The extreme slowness of the rate of falling of the drops, combined with the fact that they readily pass into vapour on reaching a warmer region, may help to explain how it is that clouds can remain suspended in the air.

Fog and Mist are clouds touching the ground. Mist is often formed over the beds of rivers in the evening, owing to the warm saturated air near the water becoming chilled by contact with the cooling earth and thus rendered unable to retain its vapour.

In a town fog, multitudes of small solid particles of dust, soot, &c., serve as nuclei around which the water vapour condenses.

Rain.—Rain is produced by the coalescence of the small water drops into larger drops, which fall more rapidly.

Hail.—The mode of formation of hail is not fully understood. The hailstones may be produced by the freezing of drops of water as they pass through a cold stratum of air.

Snow.—When the temperature of a mass of air is chilled below 0° C. the water vapour condenses into the solid form, and the aggregation of the small ice crystals produces snowflakes.

If these small crystals are formed near the ground they may be deposited as fast as they are formed. Such a deposition is called *hoar frost.*

Dew.—Dew is the layer of water that condenses from the vapour present in warm air when brought into contact with cold surfaces. The circumstances under which dew is deposited are given in Art. 174.

127. TERMS USED IN HYGROMETRY.—(*a*) The **dew-point** is the temperature at which dew is deposited. Since a deposition of moisture only takes place when the air is saturated with water vapour, the dew-point may be defined as the temperature at which the aqueous vapour actually present in the air is sufficient to saturate it. This temperature therefore varies from day to day according to the temperature and dryness of the air.

(*b*) A knowledge of the actual mass of water vapour present in unit volume of air is of less interest than that of the ratio between vapour and air.

The term **hygrometric quality** is used to express the ratio—

$$\frac{\text{Mass of vapour present in unit volume of air}}{\text{Mass of unit volume of air.}}$$

(*c*) The terms **humidity**, or **relative humidity**, or **hygrometric state** are all used in the same sense. The expression relative humidity is the most suggestive of its meaning. We have seen that there is a certain maximum mass of vapour that can be contained in unit mass of air at a given temperature, and when this amount is present the air is saturated. The air gives us the feeling of dampness or dryness according as it approaches or recedes from the condition of saturation. The amount of vapour actually present on two days might be exactly the same; but if one were a hot and the other a cold day, we should say that the air on the hot day was dry

and on the cold day moist. The term **relative humidity** indicates the ratio—

$$\frac{\text{Mass of vapour actually present in a unit volume of air at } \tau^\circ \text{ C.}}{\text{Mass of vapour which would saturate that volume at } \tau^\circ \text{ C.}},$$

τ° C. being the actual temperature of the air.

128. DETERMINATION OF RELATIVE HUMIDITY.—It is not usually necessary to actually find the mass of water vapour present in a given volume of air. It is simpler to deal with the pressure of the vapour, proceeding on the assumption that water vapour obeys Boyle's law as air does, so that if we have present in a certain limited space a mass of vapour sufficient to exert a certain pressure, and if we proceed to double the mass of vapour present in the same space, then we double the pressure, and so on. The ratio between the pressures is the same as the ratio between the masses of vapour that respectively exert those pressures. Hence for the above ratio of masses of vapour may be substituted the ratio—

$$\frac{\text{Vapour pressure at } \tau^\circ \text{ C.}}{\text{Maximum pressure at } \tau^\circ \text{ C.}}$$

This ratio is commonly expressed as a percentage.

Now the saturation or maximum pressure depends only on the temperature, and has been accurately determined for many temperatures by Regnault (see p. 417). The problem of finding the relative humidity thus generally reduces itself to finding the actual pressure of the vapour present.

Hygrometers

Various instruments have been devised for estimating the relative humidity of the air. They are called **hygrometers**.

129. CHEMICAL HYGROMETER.—In this method the mass of vapour present in a given volume of atmospheric air is determined by extracting the vapour and weighing it. This is effected by the apparatus shown in fig. 83. A continuous series of U-tubes filled with lumps of pumice-stone that have been soaked in strong sulphuric acid are connected with the top (*d*) of a large vessel A called an aspirator. At the commencement of the experiment A is filled with water. The taps *r′* and *r* are then turned, the water slowly flows out, and at the same time air is drawn through the tubes, and fills the upper part of the aspirator. During its passage through

the tubes the air deposits most of its moisture in the tube marked 6, a little in 5, and possibly some in 4. The volume of the air drawn in is very nearly equal to that of the water collected under the tap r, and the weight of the aqueous vapour is equal to the total increase of weight in the tubes 4, 5, 6. The object of the tubes

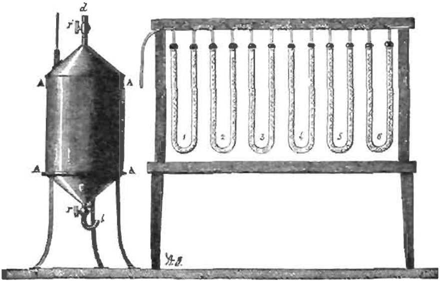

Fig. 83

1, 2, 3 is simply to absorb vapour that might come from the water in the aspirator.

Then if—

V_1 is the volume (in litres) of the air in the aspirator (*i.e.* of the water that flowed out),

m the mass in grammes of the water condensed in the tubes,

p_0 the pressure in millimetres of mercury of the water vapour in the atmosphere.

Since 1 litre of aqueous vapour at 760 mm. pressure weighs ·8017 grm., omitting corrections, we have

$$m = \cdot 8017 \times V_1 \times \frac{p_0}{760} = \cdot 001058 V_1 p_0 \text{ grm.};\ldots(A)$$

whence p_0 is readily determined.

This result is, however, only approximate for these reasons:—

(i) The air finally in the aspirator being in contact with water is saturated, while the air that entered the tubes was probably not saturated.

If p is the maximum pressure of water vapour at the temperature of the aspirator, P the pressure of the atmosphere, V_2 the volume of the air that entered at c, we have—

$$V_2(P - p_0) = V_1(P - p).$$
$$\therefore V_2 = V_1\frac{P - p}{P - p_0}.$$

This value of V_2 must replace V_1 in equation (A) above.

(ii) The temperature of the air in the aspirator may not be 0°, for which value only the above constant ·001058 is correct. If θ be the absolute temperature of the aspirator, then the reduced volume—

$$V_2 = V_1\frac{273}{\theta}.$$

Then finally

$$m = \cdot 001058 p_0 V_1 \frac{P - p}{P - p}\cdot\frac{273}{\theta}.$$

The chemical method is capable of giving accurate results, but in practice it is laborious. It has been assumed above that the aspirator and the atmosphere were at the same temperature, which remained constant throughout the experiment.

130. CONDENSATION OR DEW-POINT HYGROMETERS. —A simpler and more usual method of determining the vapour pressure in the atmosphere is based on the observation of the dew-point. When that temperature is known the vapour pressure can be at once obtained from the tables.

Thus suppose we have a mass of air at 16° C. containing water vapour. The vapour actually present is sufficient to saturate the air at some lower temperature. Let then the temperature of the damp air be lowered under the pressure of the atmosphere, which remains constant throughout. As the temperature is lowered the air gradually approaches the condition of saturation, and when a certain temperature is reached, suppose 10° C., the air is saturated with vapour, and dew begins to be deposited. The pressure of the vapour when this deposition of dew commences is the maximum or saturation pressure for that particular temperature. On referring to page 417 we see that for 10° the maximum pressure is that of 9·139 mm. of mercury. This then was the pressure of the vapour when the dew was deposited, and since this pressure did not change during the cooling, 9·139 mm. was the actual value of the pressure

of the vapour at the higher temperature of the air (16° C.) when the process commenced.

A second reference to the tables shows that the maximum or saturation pressure of water vapour at the original temperature of the air, 16° C., is 13·51 mm.

$$\text{Thus we have } \frac{\text{actual pressure}}{\text{maximum pressure}} = \frac{9·14}{13·51} = \frac{69}{100}.$$

The relative humidity was 69 per cent.

To find the dew-point several instruments are in use.

Daniell's Hygrometer.—Daniell's hygrometer consists of a bent glass tube of the form shown in fig. 84, each end terminating in a bulb. The tube contains liquid ether and ether vapour only, all the air having been expelled. In the long arm of the tube is placed a sensitive thermometer t; the bulb A is blackened and B is covered with muslin. In using the instrument the liquid ether is first passed into the bulb A, and a few drops of ether liquid are poured on to the muslin around B. This external ether at once evaporates, and cooling the bulb causes the ether vapour inside to condense in B and the liquid in A to evaporate. The temperature of A thus gradually falls, and the observer notes the reading of the thermometer t when the first film of dew appears on the blackened bulb. When the action has ceased the temperature of A rises, and the thermometer reading is again noted when the film of moisture just disappears. The mean of the two readings is taken as the dew-point; a thermometer t' mounted on the stem of the instrument indicates the temperature of the air.

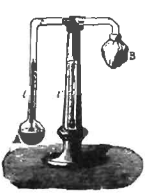

Fig. 84

There are several sources of error in this instrument.

(i) The thermometer gives the temperature of the centre of the liquid, which is higher than that of the surface, where evaporation is taking place.

(ii) Since glass is a bad conductor of heat, its outer layer where the dew is deposited is warmer than the inner layer in contact with the ether.

(iii) The presence of the ether vapour from B as well as the proximity of the observer may modify considerably the hygrometric state of the air around the bulb A.

When the air is hot and dry it is difficult to obtain indications with this instrument.

Regnault's Hygrometer. — Regnault modified Daniell's instrument in such a way as to avoid these sources of error. A glass tube D (fig. 85), closed at the bottom by a very thin and highly polished silver cap, and at the top by a cork, contains the ether. Through the cork pass a thermometer T and a tube *t* open at both ends, which reaches to the bottom of the liquid. A bent tube UV connects the top of the tube D with an aspirator, by means of which air

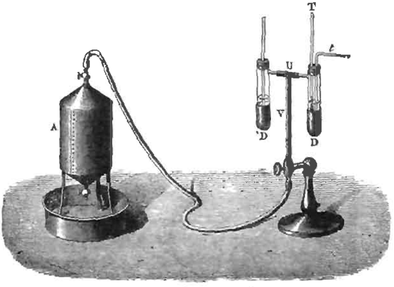

Fig. 85

drawn in through the tube *t* bubbles through the ether and passes out along the tube V. Rapid evaporation of the ether ensues, the temperature is lowered, and dew is deposited on the silver cap, which is observed through a telescope. A second tube D is made exactly like the other, but contains no ether; it serves the purpose of holding a thermometer to indicate the temperature of the air, and of presenting a bright silver surface to compare with the dull one.

The agitation of the ether and its contact with the highly conductive silver cap remove all doubt that the temperature of the thermometer is the same as that of the air around D, which, moreover, is not disturbed by the near presence of the observer. The rapidity of action is by means of the aspirator completely under control.

In a modern form of Regnault's hygrometer the second tube is

dispensed with. The tube containing the other carries a flat silver plate, while in the same plane, and nearly surrounding it, but without contact, is another plate. This enables the comparison of the two surfaces to be more readily made.

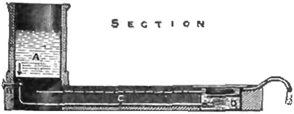

Fig. 86

Dines' Hygrometer.—This simple dew-point instrument is shown in fig. 86. It is used in this way. In the reservoir A is placed cold water, which on turning the tap B flows along the tube C into a chamber D and out through a waste pipe. The chamber D is closed at the top by a piece of polished black glass, in close contact with the under side of which is the bulb of a thermometer. The cold water chills the glass plate, and when a film of dew begins to appear upon it the thermometer is read. The water is then partially or wholly turned off, and the thermometer is again read at the moment when the dew disappears. These two temperature readings will not differ by much if the action is not too rapid, and their mean is taken as the dew-point.

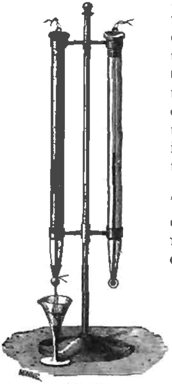

Fig. 87

The Wet- and Dry-bulb Hygrometer.—This instrument, owing to the great facility of its use, is commonly employed to determine the dew-point. It consists of two exactly similar thermometers, mounted vertically a short distance apart on a stand (fig. 87) in such a way that their bulbs are freely exposed to the air. One thermometer has its bulb covered with muslin, which is kept moistened with water by means of a cotton wick that dips into water contained in a small vessel placed somewhat below and to one side of the thermometer. The water on this bulb is continually evaporating, and this thermometer indicates a lower temperature than the other, which simply registers the temperature of the air. When the air

is dry there is a considerable difference between the readings of the two thermometers, but when the air is nearly saturated with moisture the readings are nearly the same. Such instruments are accompanied by a set of tables which interpret the indications.

The theory of this instrument is as follows. It has been shown that water exposed to the air is continually evaporating, and that the *rate* of evaporation is related to the defect from saturation of the vapour present.

Now since in evaporation heat is rendered latent and surrounding bodies are chilled, it follows that a thermometer, from the surface of whose bulb evaporation is proceeding, must fall to a lower temperature than one whose bulb is dry, and the greater the rate of evaporation the lower must be the temperature recorded. The difference between the temperatures of a dry and wet bulb thermometer thus affords indications of the rate of evaporation, and therefore of the relative humidity of the air. When the wet bulb has been cooled by evaporation of the water, if a mass of air at a higher temperature come into contact with it, the air is cooled, and parts with its excess of heat to the bulb. At the same time the air becomes charged with moisture which has evaporated, and thus heat is abstracted from the bulb. It is assumed that the air takes up sufficient moisture to saturate it and then gives place to a fresh supply, the operation being continually renewed, and that when the thermometer is registering a steady temperature the heat given to it by the air in cooling is equal to the heat taken from it by the water in evaporating. If the air when saturated with vapour remained stationary around the bulb, evaporation would be checked.

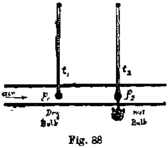

Fig. 88

To make the idea more definite, imagine the two bulbs to be placed in a tube (fig. 88), one near each end, and let a steady current of unsaturated air be maintained through the tube at such a rate that in passing the wet bulb it becomes saturated, and when saturated at once passes on. Suppose 1 grm. of air to pass when the pressure as measured by the barometer is P, and let τ_1 and τ_2 be the readings of the ther mometers, p_1 and p_2 the corresponding pressures of the aqueou vapour, L the latent heat of steam, S the specific heat of air, *d* th density of aqueous vapour compared with air.

Then omitting all small corrections we have very nearly—

(i) Mass of aqueous vapour entering the tube $\frac{p_1}{P}d$.

" " leaving " $\frac{p_2}{P}d$.

$\therefore$ Mass of water evaporated $= \frac{d}{P}(p_2 - p_1)$ grammes.

$\therefore$ Heat absorbed $= L\frac{d}{P}(p_2 - p_1)$ calories.

(ii) Mass of air lowered in temperature from τ_1 to $\tau_2 = 1$ grm.

$$\therefore \text{Heat given out} = S(\tau_1 - \tau_2) \text{ calories.}$$

$$\therefore L\frac{d}{P}(p_2 - p_1) = S(\tau_1 - \tau_2).$$

$$\therefore p_2 - p_1 = \frac{S}{Ld}(\tau_1 - \tau_2)P.$$

$$\text{or } p_1 = p_2 - \frac{S}{Ld}(\tau_1 - \tau_2)P.$$

Since approximately at ordinary temperatures about 12° C. L = 600, while S = ·237 and d = ·62 we have

$$p_1 = p_2 - \cdot000637(\tau_1 - \tau_2)P,$$

where p_2 is known from Regnault's tables; and P, τ_1, and τ_2 are observed.

To take a numerical example, suppose that on a given day the dry bulb reads 20° and the wet bulb 15° when the barometer stands at 750 mm. The pressure of saturated air at 15° is known from Regnault's tables to be 12·7 mm., which is thus the value of p_2. Then the actual pressure of the vapour in the atmosphere, i.e. p_1 = 12·7 − (·000637 × 5 × 750) = 12·7 − 2·38 = 10·32 mm. Another reference to the tables shows that this pressure is sufficient to saturate the air at the temperature 11·8°, which is therefore the dew-point.

On reference to the tables accompanying such a hygrometer (p. 416) the value of p_1 under these conditions is given as 9·7 mm., which would make the dew-point 10·9°. These tables have been drawn up by comparison with a Daniell's hygrometer, and the results obtained by the formula above only approximately agree with those of the tables. This is doubtless the fault of the formula, which is based on theoretical conditions that do not exactly represent the

real state of affairs, the assumptions above noted being only partially justified.

131. EXAMPLES.

1. Find the mass of water vapour present in 1 c.dm. of air on a day when the barometer reads 760 mm., the dry-bulb thermometer 15° C., and the wet-bulb 10° C., given the following data from the tables:—

Wet Bulb, 10°; Dry Bulb, 15°; Vapour Pressure, 6·1 mm.

By Art. 107 the mass of 1 c.dm. of water vapour at 15° C. and 6·1 mm. pressure

$$= \cdot 62 \times 1{\cdot}293 \times \frac{6{\cdot}1}{760} \times \frac{273}{288} \text{ grm.}$$
$$= \cdot 0061 \text{ grm.}$$

2. 100 *c. ft. of air at* 16° *C. yield* ·14 *oz. of water. What is the relative humidity of the air? The maximum pressure of aqueous vapour at* 16° *is* ·09 *in. of mercury. The barometer may be taken as at standard pressure, i.e.* 29·92 *in.*

The mass of 100 c. ft. of air is 8·07 lb. at 0° and 29·92 in. pressure.

∴ Its mass at 15° and under (29·92 − ·09) in. pressure

$$= \frac{8{\cdot}07 \times 273 \times 29{\cdot}83}{288 \times 29{\cdot}92} \text{ lb.;}$$

∴ the mass of 100 c. ft. of water vapour at the pressure p

$$= \frac{8{\cdot}07 \times 273 \times 29{\cdot}83}{288 \times 29{\cdot}92} \times \frac{p}{29{\cdot}83} \times \cdot 62 \text{ lb.,}$$

and this equals ·14 oz. = ·00875 lb.;

$$\therefore p = \frac{\cdot 00875 \times 288 \times 29{\cdot}92}{\cdot 62 \times 273 \times 8{\cdot}07} = \cdot 055 \text{ in.}$$

$$\text{The relative humidity} = \frac{\cdot 055}{\cdot 09} = 61 \text{ per cent.}$$

3. *The bulb of a thermometer is moistened by a solution of sulphuric acid of such strength that the thermometer reads the same as the dry-bulb instrument, viz.* 15° *C. If the hygrometric state of the air is* ·5 *and the vapour pressure of water at* 15° *C. is* 12·7 *mm., what is the vapour pressure of the solution at* 15° *C.?*

Since the thermometers read the same, no evaporation of the solution is proceeding. Its vapour pressure is therefore in equilibrium with that of the atmosphere, viz. 12·7 × ·5 = 6·35 mm.

4. If the vapour pressure of water at 0° C. is 4·6 mm., find the dew-point for air of humidity 40 per cent at 20° C., assuming that the vapour pressure is doubled for each 10° C. rise in temperature.

The saturation pressure at 20° C. is 4 × 4·6 = 18·4 mm.;

$$\therefore \text{the actual pressure is } \frac{40}{100} \text{ of } 18{\cdot}4 = 7{\cdot}36 \text{ mm.}$$

To find the dew-point, assume that the pressure-temperature curve of water vapour is represented by the equation

$$y = a + bx + cx^2,$$

where x is temperature and y vapour pressure.

Then from data given—

$$a = 4{\cdot}6,$$
$$9{\cdot}2 = 4{\cdot}6 + 10b + 100c,$$
$$18{\cdot}4 = 4{\cdot}6 + 20b + 400c,$$

whence $b = {\cdot}23$ and $c = {\cdot}023$.

$$\text{Hence } 7{\cdot}36 = 4{\cdot}6 + {\cdot}23x + {\cdot}023x^2,$$

which equation gives $x = 7$.

The dew-point is 7° C.

QUESTIONS AND EXERCISES

(The Vapour Pressures required are given in the table on p. 417.)

1. What is the meaning of the term "humidity" or "hygrometric state" as applied to the atmosphere? Give a short description of the instruments that are commonly employed for finding the state of the air with respect to moisture.
2. Explain what is meant by the dew-point. How does the dew-point show the amount of vapour in the atmosphere?
3. Describe the method of using a dew-point hygrometer to determine the hygrometric state of the air in a room.
4. Give the theory of the wet- and dry-bulb hygrometer. What are the merits and demerits of this as compared with other forms of hygrometers?
5. Find the hygrometric quality of air whose temperature is 18°, if the dew-point be 14° and the height of the barometer 735 mm.
6. The dew-point being 12° C., and the temperature of the air 17° C., find the hygrometric state of the air.
7. What is the relative humidity of the air on a day when the temperature is 20° and the dew-point 11°?
8. A stratum of air averaging half a mile in thickness contains sufficient moisture to saturate it at 16° C. If the temperature sink to 14°, find how much water will fall on a square mile of earth.
9. The relative humidity of air at 17° C. is 30 per cent; find the dew-point.
10. On a certain day the temperature of the air is 20° C., the dew-point 10° C., and the height of the barometer 752 mm. Find the mass of a litre of the moist air.
11. The dew-point on a certain day being found to be 12° C. and the temperature of the air being 16·5° C., find its humidity, having given that the maximum pressure of aqueous vapour at 12° C. is equivalent to 1·046 cm. of mercury, while that at 16° is 1·364 cm., and that at 17° is 1·442 cm.

CHAPTER XIII

HEAT AND ELECTRICITY

132. HEAT PRODUCED BY ELECTRICAL DISCHARGE. —Whenever an electrical current or discharge passes through a body heat is produced, the temperature being sometimes raised sufficiently high for the body to become luminous. In fact the highest temperature we can produce is that of the electric arc. When the current passes between carbon points the carbon is sometimes rendered soft and semi-fluid, and flint, platinum, and other substances very difficult to melt may by this means be fused, and some of them converted into vapour. All substances offer resistance to the passage of electricity, and the greater this resistance the more heat is developed by the passage.

Electrical Furnace.—Since the passage of electricity through bodies heats them, this method is now much used for heating pur-

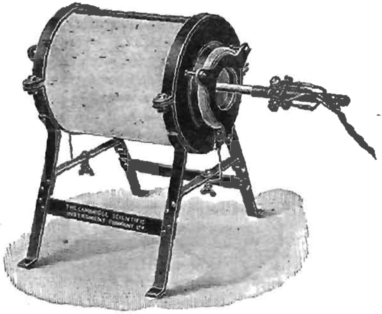

Fig. 89

poses in experimental work. Fig. 89 shows an electrical resistance furnace. The essential part is a small cylinder of porcelain round which a thin strip of platinum is wound, and the heat is developed by a current through the strip. To prevent loss of heat a very thick

lagging of asbestos is placed round the platinum strip. The whole is enclosed in a suitable case. Access is left to the porcelain cylinder at each end, and the ends may be blocked up by a plug of asbestos if desired. The temperature inside the porcelain cylinder may easily be raised to 1400° C., and this temperature may be read by a platinum resistance thermometer inserted in one end, or a radiation pyrometer may be focused on an open end. (See Chap. XVII.)

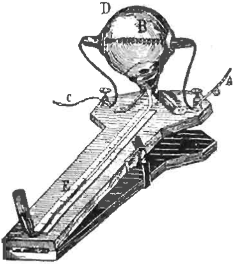

Fig. 90

Some of the earliest experiments having for their object the measurement of the heat developed by the passage of electricity through a wire were made by Riess by means of his electrical thermometer (fig. 90). A thin platinum wire B was fastened in the bulb D of an air thermometer (Art. 193), whose graduated stem E was filled with a coloured liquid. Leyden jars were allowed to discharge themselves through the wire B, and the movement of the column of liquid E indicated the comparative quantities of heat produced.

The measurements showed that the heat produced by the discharge of a jar was *proportional* to the product of the quantity of electricity Q that passed and the difference of the potential E between the two coatings of the jar. The full expression is

$$JH = \tfrac{1}{2}QE.$$

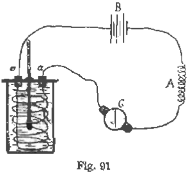

Fig. 91

133. JOULE'S LAW.—Joule first determined the law connecting the quantity of heat produced in a wire through which an electric current is passing, with the strength of the current and the resistance of the wire. Fig. 91 shows the arrangement of the circuit, consisting of a coil of wire R, a tangent galvanometer G, a set of resistance coils A, and a battery B, connected in series. The spiral R was placed within a known mass of water contained in a calorimeter, and thus the heat

produced in the wire was measured by the rise of temperature of the water. Three sets of experiments were made:—

(i) By passing the same current through the same mass of water on different occasions for different periods of time, it was proved that the heat produced is proportional to the time the current flows.

(ii) Altering the resistance of the circuit by means of the coils A, Joule changed the value of the current passing through the spiral R in different experiments, and he thus found that the heat produced in R is proportional to the square of the strength of the current.

(iii) By placing in series in the same circuit several spirals such as R, each immersed in water in a similar manner, the same current passing through them all, Joule found that the quantities of heat produced in the different calorimeters were then proportional to the resistances of the spirals they contained.

No other circumstances were found to affect the result, and Joule therefore concluded that if C represent the value of the current passing through a wire for a time t, and r the resistance of the wire, J the mechanical equivalent of heat (Chap. XIX), and H the heat produced, then

$$JH = C^2rt = CEt = \frac{E^2}{r}t.$$

This is Joule's law.

Since the quantity of electricity Q that passes is equal to the strength of the current multiplied by the time, $Q = Ct$; and by Ohm's law $Cr = E$, therefore

$$JH = C^2rt = Cr \times Ct = QE,$$

a result which may be compared with that of Art. 132.

The above equation is expressed for absolute units.

For practical units, if H = the heat developed measured in calories, C the current in amperes, R the resistance in ohms, and t the time during which the current passes measured in seconds, then

$$H = C^2Rt \times \cdot 24.$$

Example.—A current of ·25 ampere is passed for 5 minutes through a wire whose resistance is 2 ohms. Find the number of calories dissipated by the wire.

$$\begin{aligned} H &= C^2Rt \times \cdot 24 \\ &= \cdot 0625 \times 2 \times 300 \times \cdot 24 \\ &= 9 \text{ calories.} \end{aligned}$$

Heat from Induced Currents.—When a piece of metal, whether in the form of a mass, plate, or wire, is moved near a magnet, electric

currents are produced in the metal, and these currents produce heat. The mass of metal thus moved rises in temperature. The currents that are produced are transient, lasting only as long as the motion lasts, and their strength also changes very rapidly. But whether the current is transient or continuous, the quantity of heat produced is that given by the above law.

134. VARIATION OF ELECTRIC RESISTANCE WITH TEMPERATURE.—If when a steady current is passing round the circuit (fig. 91) the calorimeter and wire R be raised in temperature, the current indicated by the galvanometer is found to diminish. If the electromotive force of the battery has remained constant, the effect must be due to an increase in the resistance of the wire R owing to its increased temperature. A change of electrical resistance with temperature is found in most substances.

(i) **Metals.**—The electrical resistance of metallic conductors is greater at high than at low temperatures. All the more common metallic elements, except the magnetic metals, have a resistivity at 100° C. about 40 per cent greater than at 0° C.

The following table is taken from a paper by Fleming (Proc. Roy. Inst.):—

Electrical Resistivity

Metal.	Resistivity in C.G.S. Units at 0° C.	Percentage Increase, 0° C. to 100° C.
Silver	1468	40·0
Copper	1561	42·8
Gold	2197	37·7
Iron	9065	62·5
Platinum	10917	36·7
Mercury	94070	38·9
German silver	29982	2·73
Platinoid	41731	3·1
Platinum-iridium ...	30896	8·2
Manganin	46678	0·0

This table illustrates the great difference between elements and alloys in the value of the temperature coefficient. For standard coils and for the coils of resistance boxes, in which it is desirable to have but little variation, it is usual to employ manganin or German silver. Resistivity is the resistance of unit cube.

Dewar and Fleming examined the resistivity of many metals at temperatures down to approximately − 200° C. The decrease

of resistivity in all cases diminished as the temperature was lowered, and the curves which represent the variation of resistivity with temperature indicate that at about $-250°$ C. the electrical resistance offered by a wire of most pure metals would be zero. Alloys show no approximation to this condition.

For several metals, e.g. copper, silver, and German silver, the resistances r_τ at $\tau°$ C. and r_o at $0°$ C. are connected by the linear law,

$$r_\tau = r_o(1 + a\tau),$$

with fair accuracy for values of τ not greatly different from ordinary temperatures.

In no case, however, is this linear law exact, and in some cases, e.g. iron, it is decidedly inexact, so that it is generally necessary to use the formula

$$r_\tau = r_o(1 + a\tau + b\tau^2).$$

The constants a and b are determined by measuring the resistance of the material accurately at $0°$ C. and at other temperatures not close to $0°$ C., placing in the formula the values of r_τ thus obtained, and solving the equations thus given for a and b. When these constants are known for a given wire, the temperature of any enclosure in which the wire is placed may be fonnd by measuring its resistance in the enclosure and placing the value for r_τ thus obtained in the above formula. Callendar has made a special study of platinum, and has developed a system of measuring temperature in this way (Chap. XVII).

(ii) **Electrolytes and Bad Conductors.**—Substances, e.g. water, in which the passage of the electric current is accompanied by their chemical decomposition are called **electrolytes**, and in such substances the electrical resistance is diminished by rise of temperature. The same effect is observed with glass, which, when very hot, will conduct electricity very well, whereas when cold it is one of the worst conductors known. Carbon is another interesting example, owing to its use for filaments in incandescent lamps; its resistance when white-hot is only about half as great as when cold, while its resistance at $-200°$ C. was found by Dewar to be considerably greater than at $0°$ C.

Relation between Thermal and Electrical Conductivity.—Forbes first pointed out that good and bad conductors of heat were also respectively good and bad conductors of electricity, and that the table of metals drawn up in the order of their thermal con-

ductivities was the same as the table showing the order of their relative electrical conductivities. Wiedemann and Franz went further, and said that there was a definite simple ratio between the two conductivities.

The results of experiments published by F. Weber in 1880 were not favourable to any such simple relation, and Weber suggested that the apparent proportionality observed by Wiedemann and Franz was due to the fact that the metals they experimented on, viz. copper, iron, and brass, have nearly the same specific heat of unit volume—a quantity which plays an important part in such investigations. Later experiments by Kirchhoff and by Lorenz, however, appear to confirm Wiedemann's conclusion that the ratio $\frac{\text{conductivity of a metal for heat}}{\text{conductivity of the same metal for electricity}}$ has the same value in different metals. The following table illustrates the supposed connection:—

	Copper.	Zinc.	Iron.	German Silver.
Relative thermal conductivities (Neumann)	1108	307	164	109
Relative electrical conductivities (Matthiessen)	1108	322	187	86

135. THERMO-ELECTRICITY.—Let two wires or bars of different metals, A and B (fig. 92), preferably antimony and bismuth, be fastened together at one end, and have the other ends *cd* connected by copper wires to the terminals of a delicate galvanometer G. If the junction be now warmed, a deflection of the galvanometer needle at once takes place, indicating that an electric current is passing round the circuit, and the indications of the galvanometer show that up to a certain point the higher the temperature of the junction the stronger the current. If, however, the temperature be raised above a certain point the current begins to decrease.

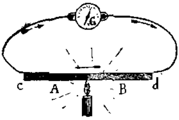

Fig. 92

If the ends *cd* be warmed simultaneously and equally with the junction no deflection takes place. If ice be applied to the junction while the temperature of *c* and *d* remains that of the atmosphere,

the direction of the current is reversed. The wires connecting the points *cd* play no part in the production of the current, the effect being the same as though *c* and *d* were in contact. Thus in a circuit composed of two different metals, if one junction be hotter than the other an electromotive force is brought into existence at the junction, and an electric current is produced in the circuit. Such currents are called **thermo-electric currents**, because they are produced and *maintained by heat. Any pair of metals similarly treated give* a similar effect in greater or less degree. Hence we may have **thermo-electric "couples"** of various metals, and by forming couples with some one metal and each of the other metals in turn Becquerel formed a thermo-electric series, showing the relative electromotive forces set up with a given difference of temperature between various metals. The term **thermo-electric force** is used to *denote the electromotive force set up in this way.*

Variation of Thermo-electric Force with Temperature.—The dependence of thermo-electric force upon the temperature of the junctions can be observed by *arranging a circuit in the manner* shown in fig. 93. A steady current is maintained in a circuit of high resistance ABC, a portion of which may conveniently consist of the wire AB of a Wheatstone's bridge. By this means *the potential differences between* B and different points along AB are comparable. The thermo-electric circuit previously described (fig. 92) is adjusted to this as a shunt-circuit in the manner shown in the figure—D being a sliding contact. For purposes of measurement the thermoelectric junctions are placed in baths, whose temperature can be regulated and measured, and for each pair of temperatures a position of D is found, which gives no deflection of the galvanometer when both circuits are closed. When that is the case the difference of potential between the points B and D due to the *thermo-electric couple is the same as that due to the battery.* This may be found in absolute measure by a separate experiment in

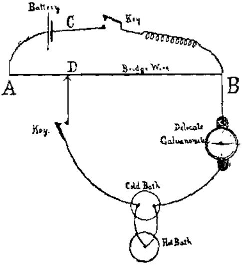

Fig. 93

which a standard cell is used to establish a known difference of potential between two points on the bridge wire.

As the temperature of the warm bath is gradually raised the thermo-electric force at first increases; at a certain temperature called the **neutral point** of the two metals it reaches a maximum value, and then commences to decrease. The neutral point for a copper-iron couple is about 270°. If the heating be sufficiently continued, the thermo-electric force falls steadily to zero, and then changes sign, the current produced under these circumstances being in the opposite direction to that produced at first. This last phenomenon is known as **thermo-electric inversion**, and takes place when the mean of the temperatures of the junctions is the neutral point.

According to Tait the thermo-electric force of two metals is connected with the temperatures of the junctions between 0° C. and 600° C. as in the following formula:—

$$E = M\left\{\theta_1 - \theta_2\right\}\left\{\theta_0 - \frac{\theta_1 + \theta_2}{2}\right\}$$

where θ_0 θ_1 θ_2 are the absolute temperatures respectively of the neutral point, the hot junction and the cold junction, and M is a constant peculiar to each pair of metals.

To give a practical idea of thermo-electric force (i.e. the electromotive force of a thermo-electric couple) we may remark that with a copper-iron couple having one junction at 0° C. and the other at 100 C. the thermo-electric force is about $\frac{1}{800}$ of the E.M.F. of a Daniell's cell, and with a bismuth-antimony couple under the same conditions about seven times that value.

It is manifest that when once the values of E, M, and θ_0 have been determined for any pair of metals, such an arrangement may be used to measure temperature. (See Art. 195.)

Tait introduced the term **thermo-electric power** to denote the rate at which the thermo-electric force of any couple is varying with the temperature of that junction which is changing its temperature, and expressed his results in a diagram (fig. 94). In this diagram the abscissæ represent temperature, and the ordinates thermo-electric power for the metals iron, copper, and zinc, with reference to lead. In such a diagram thermo-electric force is represented by an area. Thus the area AEFD represents the thermo-electric force of an iron-zinc couple with its junctions at 0° and 100° respectively, and the area AHKD represents the thermo-electric force of an iron-copper couple within the same limits.

Fleming continued the investigation for temperatures between 00° C. and −200° C., and his lines of thermo-electric power for he metals iron, zinc, copper, and platinum, with reference to lead,

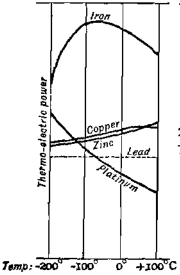

Fig. 95

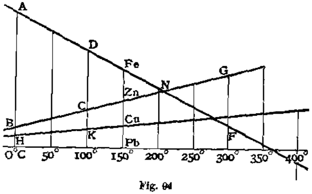

Fig. 94

are shown in fig. 95. It will be observed that at the lower temperatures some of the lines are not straight. He found that there was a general tendency for the lines to curve in such a manner as to indicate that the thermo-electric power would probably become zero at or near the absolute zero of temperature.

136. THE THERMOPILE.—If several thermo-electric couples be joined together in series, as indicated in fig. 96, the total thermo-electric force is correspondingly multiplied.

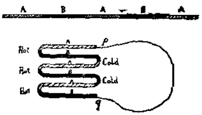

Fig. 96

If the terminals pq be joined by a wire, and one set of junctions warmed, a current flows round the circuit. Such an arrangement can be made to take any convenient shape, and in the thermopile (fig. 97) the bars are packed in layers of the form shown, the whole forming a cube with the junctions at two opposite faces, and the metals so connected that if they were sufficiently ductile they could be pulled out into a straight line as indicated in fig. 96.

The thermopile when in use has the terminals of the metals connected, as shown, to a delicate galvanometer. If a reflecting galvanometer be employed, its sensitiveness is so great that a very small

difference of temperature between the faces of the thermopile gives a measurable current. For very small currents the temperature

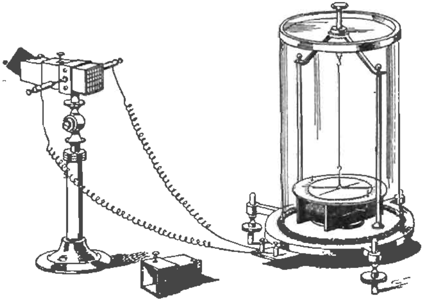

Fig. 97

difference may be taken as proportional to the current. This was the apparatus used by Melloni for his researches on radiation (Chap. XVI).

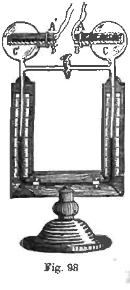

Fig. 98

137. PELTIER EFFECT.—It was discovered by Peltier that when a current of electricity passes through a junction of two metals the junction is either heated or cooled according to the direction of the current. A current passing from a rod of antimony to a rod of bismuth heats the junction of the metals; if the current pass in the opposite direction the junction is cooled. The direction of the current which produces the cooling is that of the thermo-electric current which would be produced if the junction were heated.

Peltier's apparatus for demonstrating this phenomenon consisted of a differential air-thermometer (fig. 98) into the bulbs of which were inserted bismuth-antimony couples AB and A′B′, which were connected with wires leading to a battery.

When a feeble current was passed from B to A, or from B′ to A′, the air in the corresponding bulb contracted. When the current was passed in the opposite direction the air expanded.

When A was joined to A′, B to one pole of a battery, and B′ to the other, so that the current passed round the circuit BAA′B′, the air in C contracted, while that in C′ expanded, the effect obtained being the sum of the previous separate effects.

Le Roux placed the two pairs AB and A′B′ in water contained in separate calorimeters, and by employing delicate thermometers was able to measure the heat evolved or absorbed in the process; and it was found that the heating or cooling effect is proportional to the strength of the current.

138. THOMSON EFFECT.—Sir William Thomson in 1846 discovered another most interesting fact as to the relations of heat to the electric current. If a wire be made hotter at a point A than at a neighbouring point B, and an electric current then passed along it, the position of maximum temperature will be carried from A either towards B or from B according to the direction of the current. When *an electric current passes from hotter to colder or from colder to hotter parts of the same wire it carries heat or cold with it.* The phenomenon has thence been called the **electric convection of heat**. The effect is opposite in copper to that which shows itself in iron.

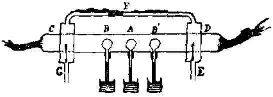

Fig. 99

One of the forms of Sir William Thomson's apparatus is shown in fig. 99. CAD was a tube of thin sheet iron containing at the centre of its length an air thermometer A and similar thermometers B and B′ on each side of A. Cold water circulating through a system of pipes EFG maintained the ends C and D at a constant low temperature. The ends of the tube terminated in bundles of wires, by means of which the tube was connected with an electrical circuit in which a strong current was flowing. The tube was heated by the current so that the temperature indicated at A was about 76° C. When the current passed from C to D the thermometer B′ indicated a lower temperature than B, and when the current was reversed the liquid column in B′ quickly fell, while that in B quickly rose.

QUESTIONS

1. What is Joule's law of the heat produced in an electric circuit, and how is it proved?
2. Two wires whose resistances are in the ratio of 2 to 3 have currents passing through them whose strengths are in the ratio of 3 to 2. Compare the quantities of heat produced per second in the wires.
3. Describe the Peltier effect and the Thomson effect.

CHAPTER XIV

CONDUCTIVITY

139. TRANSMISSION OF HEAT AND TEMPERATURE.—A general idea as to the conducting power of substances may be obtained by touching them, at ordinary temperatures, with the warm hand. If they chill the hand rapidly, as is the case with metals, they are good conductors; if they do not, as is the case with wool, silk, felt, and similar materials, they are bad conductors.

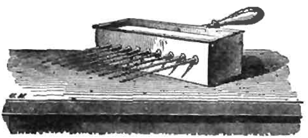

Fig. 100

A useful apparatus for a preliminary study of conductive power is that of Ingenhausz, shown in fig. 100. Several rods of different metals, but of the same size and with the state of their surfaces as nearly as may be in the same condition of polish, have each one end fixed in exactly the same manner through the side of a trough. The portions outside the trough are thinly coated with wax, and the trough is then filled with some hot liquid, such as oil or water, whose temperature is maintained constant. The heat is conducted along the rods and melts the wax.

In the early or variable stage of the experiment, while the melting is advancing along the rods, the rate at which the melting proceeds is unequal. It is faster, for instance, along a rod of bismuth than along a rod of iron. When the melting ceases to advance along the rods and the permanent stage is reached, the lengths along which

the wax is finally melted are also different for different rods, being greater, for instance, with iron than with bismuth.

The rates of melting of the wax must thus be carefully distinguished from the lengths finally melted. *During the variable stage* of the experiment a "wave of temperature" is passing along each bar.

The wax melts when its temperature is raised to its melting-point, so that the course of the melting of the wax marks the propagation of this wave of temperature. During this process the heat is changing the thermal condition of the bar; it is raising the temperature of the successive layers as it reaches them, and the greater the quantity of heat that is required to effect this change, the longer time, if no other cause affect the result, does the process occupy, and the slower is the rate of propagation of the wave. For instance, it requires seven times as much heat to warm the first cubic centimetre of an aluminium rod as it does to warm equally the corresponding *part of an iron rod, so that unless the heat were passed on from* layer to layer of the aluminium rod seven times as fast as along the iron rod, the wave would proceed more rapidly along the iron rod.

The process going on in the bar during this stage is called the **diffusion** of heat or **thermometric conduction.** It is evident that the rate of propagation of the wave is affected by the thermal capacity of the substance.

After this variable stage has been passed a permanent stage is reached, in which the heat flows through the substance of the rod without altering the temperatnres of the various parts aud is steadily dissipated from the surface of the bar. The heat then effects no change in the thermal condition of the suhstance; the only process going on is that of the transference of heat from layer to layer of the bar. This process is **conduction** of heat, and the conductivities of tbe rods can be shown to be proportional to the squares of the lengths along which the wax has been melted. The method *forms a convenient means of comparing the conductivities of metals.*

140. CONDUCTIVITY AND DIFFUSIVITY.—**Conductivity** is the numerical measure of conduction.

This subject has been investigated mathematically by Fourier. Fourier's theory supposes that heat passes from one molecule to another by radiation just as it does between two larger masses. A hotter molecule radiates heat to a colder one, the quantity thus communicated decreasing rapidly as the distance between the molecules increases, being proportional to the difference of temperature

between them, which is always small, and independent of the absolute temperature of the molecules. Although the third condition is not based on experimental evidence, the results of Fourier's theory correspond well with experience.

An important case is that in which heat is propagated through an indefinitely large mass of solid.

Imagine a large cube of conducting material, of which one face G is kept hot and the opposite face B cold (fig. 101). Consider a small area C in the middle of the block, having its faces parallel to G, B. The flow of heat through the lamina C is perpendicular to its faces, and there is no loss from the edges of the lamina, because those edges are at the same temperature as the remainder of the solid in the same plane. Then Fourier's theory shows that the quantity of heat H that passes through the lamina C is directly proportional to—

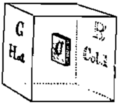

Fig. 101

(i) the area A of the lamina.

(ii) the difference of temperature $\tau_1 - \tau_2$ existing between the opposite faces.

(iii) the time t.

(iv) the conductivity k of the material of the plate;
and inversely proportional to

(v) the thickness l of the lamina.

Thus $$H = kA\frac{\tau_1 - \tau_2}{l}t.$$

If A and l are each made equal to unity the lamina becomes a cube. If, further, the difference of temperatures $\tau_1 - \tau_2$ be one degree and the time t one second, then $H = k$, which gives the following definition: *The conductivity of a substance is measured by the quantity of heat that flows in unit time through unit area of a plate of that substance whose thickness is unity, when the difference of temperature between the faces is also unity.*

The term **calorimetric conductivity** is sometimes employed for conductivity in order to distinguish it from thermometric conductivity or diffusivity.

Diffusivity is the numerical measure of diffusion, i.e. the rate of diffusion of heat through a substance. The mathematical treatment of the subject, which cannot be given here, shows that when a solid is brought into contact with a source of heat, the heat diffuses

through its mass according to a law whose expression involves the conductivity of the substance, and, as indicated above, a factor involving the thermal capacity. The two processes of diffusion and conduction of heat are closely related. The difference between them is due to the fact that different substances have different thermal capacities. If all bodies had the same thermal capacity the relative rates of propagation of a wave of temperature through them would measure their relative conductivities.

The rate of diffusion of temperature is slower for a body of higher thermal capacity and faster for a body of lower thermal capacity. If two substances are of equal conductivity their diffusivities are inversely proportional to their thermal capacities.

It is usual in experiments on conductivity to compare equal volumes rather than equal masses of different substances. If, then, c be the thermal capacity per unit volume (specific heat × density) and k the conductivity as above defined,

$$\text{Diffusivity} = \frac{k}{c} = \frac{\text{conductivity}}{\text{thermal capacity of unit volume}}.$$

141. DETERMINATION OF CONDUCTIVITY.—Clement in his experiments to determine the value of the conductivity employed a sheet of copper, 1 sq m. in area and 2·5 mm. thick, placing one face in contact with steam at 100° C. and the other in contact with cold water at about 28° C. Then H the quantity of heat that passed through the plate in a given time t was known from the rise of temperature of the cold water, and the formula gave—

$$H = k \times 10000 \times \frac{72}{\cdot 25}t;$$

whence k was determined.

The value obtained for the conductivity was only about $\frac{1}{200}$ of that now known to be correct. The failure of the experiment was due to the fact that the temperatures of the two faces of the plate were very different from the temperatures of the steam and cold water with which they were apparently in contact.

Peclet repeated these experiments, lessening the differences of temperature between the faces, and stirring the water very vigorously. He obtained for copper a value thirty times as great as that of Clement, but his results for good conductors are, nevertheless, useless from the cause indicated above.

By employing plates of different thickness, and exposing their faces to different temperatures, he, however, established experimen-

tally the law embodied in Fourier's formula that the flow of heat across a plate varies directly as the difference of temperature between the faces and inversely as the thickness of the plate.

The difficulty experienced by Clement exists to a marked degree in boilers. A boiler plate is exposed to hot gases on one side and to comparatively cold water on the other. Recent investigations show that there adheres to the one side a thin film of hot gas probably about $\frac{1}{40}$ in. thick, and to the other side a film of water of about the same order of thickness. The resistance of the gaseous layer to the conduction of heat is very great, forming, according to Hudson's experiments, about 97 per cent of the whole resistance to the passage of the heat. Its removal may be partially effected by causing the hot gases to move over the plate at a high velocity, a remedy which modern practice is adopting. The film also becomes thinner when the temperature of the gases is very high. The existence of this film may be demonstrated by boiling water in a paper vessel held over a flame. As the paper, though a bad conductor, remains unburned, it is clear that its temperature remains comparatively low. Inspection shows that the flame does not come into contact with the vessel.

142. Where slabs of some thickness are available the following method avoids the difficulty. ABCD (fig. 102) represents the slab of

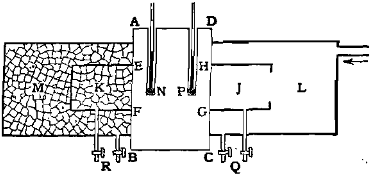

Fig. 102

material having an ice chamber M on one side and a steam chamber L on the other. Smaller cylinders J and K abut upon the central parts of the sides of the slab, and thermometers or thermo-couples N and P are inserted in the slab along its central line a measured distance apart. Steam is passed continuously into the connecting cylinders L and J, the disconnected cylinders M and K being packed with pieces of ice. The cylinders J and K as well as the portion EFGH of the slab being

thus each surrounded with material at the same temperature as itself, there is no loss of heat from the sides, and the lines of flow of heat through the central portion of the slab EFGH are straight. And the temperatures being taken at the points N and P within the slab, *there is no surface film to consider.* The mass of steam condensed in J and the mass of ice melted in K are ascertained by the mass of water drawn off through the taps Q and R, and this gives the quantity of heat transmitted through the cylinder EFGH whose dimensions are known. The temperature gradient is known from the indications of the embedded thermometers. Thus *all the quantities of the equation of Art.* 140 *are known except* k. *By this method,* usually known as the *guard-ring method,* Berget has obtained the following values of k—for copper 1·04, iron ·159, brass ·26 in C.G.S. units.

143. MEAN AND TRUE COEFFICIENTS OF CONDUCTIVITY.—In such measurements as those indicated above, it is clear that the coefficient k obtained is a mean value between the temperature limits employed. If k changes with the temperature, it has a separate "true" value for each temperature. *It is therefore necessary to distinguish between the mean and true values of* k. *The true conductivity at* $\tau°$ is the value obtained for k from the expression $k = Hl/At(\tau_1 - \tau_2)$ when τ_1 and τ_2 are indefinitely near to $\tau°$. If l and t be also indefinitely small the expression of Art. 140 becomes in the notation of the calculus $H = kA\frac{d\tau}{dl}dt$; $\frac{d\tau}{dl}$ is called the **temperature gradient**.

144. FORBES'S EXPERIMENTS.—*Among* the earliest measurements of a thoroughly reliable character were those of Forbes, the principle of which we now attempt to explain.

Consider a bar AB (fig. 103) having one end A maintained at a steady temperature, suppose 10° C., and the other end B at 0° C., the temperature of the surrounding air being also 0° C. Imagine a groove filled with mercury to exist along the upper surface of the bar, and ten thermometers to be placed therein in such positions that they read successively 10°, 9°, 8°, &c., to 0° C., each thermometer being very nearly at the centre of a certain length, whose mean temperature it indicates.

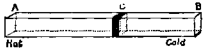

Fig. 103

Heat is pouring into the bar at A, and since the bar gets no hotter or cooler this heat is all dissipated at the surface of the bar. Fix the attention on a lamina C. It is clear that less heat is passing through C than entered at A, because some has been dissipated at the surface between A and C. The quantity of heat that passes through C is the quantity H of the formula, and its measurement is the object to be accomplished. Suppose there are four thermometers between

C and B reading respectively 4°, 3°, 2°, and 1°, the length of their sections being respectively a, b, c, d. Then if h_1 be the quantity of heat dissipated per second from unit length of a bar at 4° when placed in an enclosure at 0°, the heat dissipated per second in this section is ah_1 units. Similarly, if h_2 be the quantity of heat dissipated per second from unit length of a bar at 3°, then the heat dissipated per second from this section is bh_2 units, and so on. Thus the total heat that passes through C would be

$$ah_1 + bh_2 + ch_3 + dh_4.$$

The quantities a, b, c, d are easily measured. The quantities h_1, h_2, &c., are ascertained by a separate experiment thus: Let the bar be heated to 10° and allowed to cool in an enclosure at 0°, its temperature being observed, say, every second during the whole time of its cooling. The fall of temperature, mass of unit length, and specific heat of the bar being known, we can calculate the quantity of heat that leaves unit length of the bar in one second during each stage of the cooling process. Suppose it is found that each unit of length when at 4° parts with h_1 units of heat per second, at 3° it parts with h_2 units per second, and so on down to 0°. Since this small bar in cooling passes successively through all the temperatures at which the different portions of the long bar were maintained in the first experiment, the quantities of heat thus calculated are the same as the quantities of heat h_1, h_2, &c., that left the long bar per second at the same temperatures in the first experiment. The sum of the terms ah_1, bh_2, &c., can now be obtained, and H the whole quantity of heat passing through the layer C is known.

The quantity $\frac{\tau_1 - \tau_2}{l}$ may be obtained by placing thermometers exactly at the boundary planes of the layer C, noting the temperatures τ_1 and τ_2, and measuring the thickness l.

If such a set of readings be taken for positions all along the bar, the data are obtained for a number of values of k, viz.: One for every section of the bar, and as these sections are at different temperatures, the experiments serve to decide the further question whether the conductivity varies with the temperature.

The experiment was not of course carried out as above described. The description is merely intended as an attempt to make the method understood without the aid of mathematics.

Forbes experimented on two iron bars, of which the principal one was 8 ft. long and 1¼ in. square. In one set of experiments the bar had a semi-polished surface, while in another set it was pasted over with thin paper. His apparatus is shown in fig. 104. One end of the bar AB was about at the temperature of the air. The other end was maintained at a high temperature by means of a cast-iron cup containing melted lead or solder kept fluid by means of a gas furnace. This cup was finely adjusted to the bar by filing. It was found that by careful attention the temperature of the molten liquid could be maintained fairly constant during the time each experiment lasted, which was from 6 to 10 hours. Ten thermometers were inserted in mercury contained in small holes in the bar at distances varying from 3 in. to 8 ft. from the hot end, and they as well as

the bar were carefully screened from radiation proceeding from the source of heat.

The two quantities to be determined are H, the whole flow of heat, and $\frac{\tau_1 - \tau_2}{l}$. The latter quantity, when the layer is very thin, becomes $\frac{d\tau}{dl}$; it gives the variation of temperature with distance at any point, and the conductivity is proportional to $H \div \frac{d\tau}{dl}$.

From the readings of the ten thermometers Forbes drew a temperature curve *abc* (fig. 104), in which the abscissæ were the distances from the hot end, and the ordinates the excess of temperature at those points of the bar over that of the air. The curve was very nearly a logarithmic curve. It served to give the temperature at any point of the bar, and

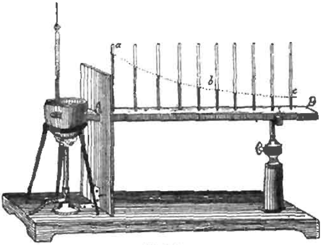

Fig. 104

the value of the tangent $\frac{d\tau}{dl}$ at any point of the curve gave the variation of temperature with distance at the corresponding point of the bar.

He then heated a short bar to the temperature of the melted lead or somewhat above, and, allowing it to cool, took its temperature at frequent intervals. From this he drew a curve representing its rate of cooling, taking for abscissæ the time and for ordinates the excess of temperature above that of the air.

At any point of this curve the value of the tangent $\frac{d\tau}{dt}$ represented the rate at which the temperature was falling, from which the rate at which the heat was leaving the bar at the temperature corresponding to that point was known.

Since the second curve gave the rate at which heat was leaving the bar at any temperature, by integrating between any two assigned values τ_1 and τ_2 the whole loss of heat from that portion of the

bar which was between those limits of temperature became known. The quantity H may also be obtained thus: Take as abscissæ l_1, l_2, &c., different lengths along the experimental bar. The excess of temperature τ at each of these points is known from the curve of temperatures; these excesses of temperature are the ordinates of certain points on the second curve, and the tangents $\frac{d\tau}{dt}$ at the points thus formed give the rate at which heat is leaving the bar at those points.

With l_1, l_2, &c., as ordinates, and the corresponding values of $\frac{d\tau}{dt}$ thus obtained, construct a curve. From the area of this curve, which is very nearly a logarithmic curve, we obtain the total escape of heat from the bar or from any part of it. The loss per unit of time on the cooler side of any given layer is represented by the area beyond the corresponding ordinate to the point where $\frac{d\tau}{dt}$ is zero.

We give the readings obtained by Forbes for two points on the bar, and the final reduced values of k.

Actual Temperature in C°.	Excess above Temperature of Air.	Values of $\frac{d\tau}{dt}$.	Flux (H) corresponding to $\frac{d\tau}{dt}$.	$H \div \frac{d\tau}{dt}$.	k in C.G.S. Units.
25	12	11	·15	·0136	·18
50	37	40	·52	·0130	·17

The numbers in the fifth column are proportionate to the conductivity at the temperatures given. To reduce them to absolute values they must be multiplied by the values of the specific gravity and the specific heat of the substance of the bar. The further reduction to C.G.S. units gives the values shown in column six.

145. EXPERIMENTS OF WIEDEMANN AND FRANZ.—The arrangements used in these experiments are indicated in fig. 105. The experimental bar AA′, which was half a metre long, thin, and coated with silver, was placed in a glass cylinder C, one end A projecting into a chamber E through which steam was kept circulating, while the other end was supported on a projection from the metal plate D which formed the end of the cylinder. The temperature of different portions of the bar was ascertained by means of a thermo-electric couple B (Art. 195) which clasped the bar and which could

be moved into any required position by means of the glass rod F. This method of obtaining the temperatures is preferable to the use of mercury thermometers, as the mercury is liable to move with sudden jerks; but the rods employed in these experiments were short, and the range of temperature was not great, the effect of electroplating the rods being to check the radiation to a very great extent. The results showed that the temperature of the experimental bar at equidistant points on its length, beginning from the heated end, exceeded the temperature of the enclosure by amounts forming a decreasing geometric progression. This result is in accord with Fourier's theory.

Wiedemann and Franz also concluded from their experiments that the thermal conductivities of metals are in the same ratio to each other as the electrical conductivities (Art. 134). For general results see the table on p. 415.

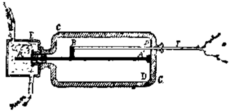

Fig. 105

Recent measurements of conductivity have usually been deduced from observations during the variable stage when a wave of temperature is passing along the bar. The theory of the method is difficult, and we can only here indicate the course of the experiments.

Ångström took long bars of metal and caused a succession of temperature waves to pass along them by alternately strongly heating and cooling one end. The period of a complete wave was about 24 minutes. The passage of the wave along the bar was indicated by a series of embedded thermometers as in Forbes's experiments. From the series of curves thus obtained the value of the diffusivity was calculated. The conductivity is then deduced by multiplying the diffusivity by the thermal capacity of unit volume of the bar.

The following figures have been obtained for iron and copper:—

	Forbes.	Neumann.	Ångström.	Berget.	Callendar.
Iron	·209	·164	·199	·159	·11
Copper	1·08	1·108	1·027	1·04	—

The variation in the figures is due to the difficulty of the experiments, to differences in the quality of the material used, and to

difference in the limits of temperature within which the determinations were made.

146. DIFFUSIVITY: UNDERGROUND TEMPERATURES.—The method of Ångström was applied by Lord Kelvin and Forbes to the rocks that constitute the earth's crust by observations on thermometers immersed to different depths. Waves of temperature are started downward by the summer heating and winter cooling of the surface, and the period of such waves is of course a year. The waves appear to die away at a depth of about 50 ft., but there is considerable variation in the numerical results obtained, owing to the differences between the heating and cooling in different seasons and the different character of the material near the surface. Below this depth the mean temperatures increase with the depth, the rate of increase being on an average 1° C. for every 110 ft.

Some recent observations in a deep boring in Virginia showed a rate of rise of temperature increasing with the depth from 1° C. every 160 ft. near the surface to 1° C. every 110 ft. at a depth of about 4000 ft.

This gradual rise of temperature with gradually increasing depth shows that there is a flow of heat from the interior to the surface; and on the data available as to the rate of this flow, Lord Kelvin calculated that it could not be more than about 200 million years since the earth was in a molten state. But the recent discovery of the production of heat by radium and the disintegration of radioactive substances is leading to a modification of these figures, for radioactive substances have been found to be widely diffused in sensible quantities in the earth among the older rocks, and the production of heat from this source is so considerable as to point to the conclusion that the earth has been in much the same state as now for several hundred million years.

147. **Variation of Conductivity of Metals with Temperature.**—Forbes concluded from his experiments that the thermal conductivity of metals decreases with rise of temperature, but Tait has shown that this conclusion, which depended on the assumption that the specific heat is constant, is not justifiable. Ångström and Thalen investigated the matter, but the results as yet attained are somewhat contradictory. It appears, however, that the simple proportionality that was formerly supposed to exist in this respect between electrical and thermal conductivity is not established. (See Art. 134.)

148. METHODS FOR BAD CONDUCTORS.—The methods described above are inapplicable to bad conductors, because with

such substances the heat lost by radiation and convection is very large as compared with that conducted through the mass. Peclet's method has been described above. It is fairly good for bad conductors, but the loss of heat from the edges is a defect. Ayrton and Perry, therefore, following out a hint of Lord Kelvin, heated a sphere of porphyritic trachyte (building stone) in a bath maintained for a long period at a constant temperature, and then cooled it by immersing it in a rapid stream of cold water. The outside being thus at a constant lower temperature, the rate of fall of temperature at the centre of the ball was observed in this way. At the centre of the sphere was a small cavity containing mercury, into which dipped a copper-iron thermo-electric junction attached to two very fine leading wires that were cemented into the stone. The other copper-iron junction was immersed in a bath the temperature of which was continually adjusted, so that a galvanometer in the circuit indicated as nearly as possible no current, under which circumstances a thermometer immersed in the bath gave the temperature of the centre of the sphere. In Fourier's work on conduction an equation is obtained for the temperature of a point at x centimetres from the centre of a homogeneous globe, and by substitution in this of the numerical quantities observed the value ·0059 was obtained for k.

A modification of Forbes's method has been employed by Lees. He took two metal bars of the same material and diameter and placed them in a line, with a disk of the badly conducting substance, also of the same diameter, between their adjacent ends. One end of one bar was then heated, and by means of thermo-electric couples the distribution of temperature along the two bars was observed with the disk first in and then out. The ends of the bars were amalgamated with mercury to ensure good contact. The conductivity was calculated by Forbes's formula. Disks of various thickness were employed. The values obtained for the conductivity were—

Crown glass, ·0024.
Rock salt, ·014.
Shellac, ·0006.
Quartz along the axis, ·03; perpendicular to axis, ·016.
Iceland spar along the axis, ·01; perpendicular to axis, ·0084.

In another series of experiments by Lees a pile of small disks (fig. 106) was made, A, B, and C being of copper, E the substance to be experimented on, and D a flat coil of wire through which a current

of electricity was passed, and in which therefore heat was generated at a known rate. When the steady state was reached this heat was dissipated from the surfaces of the pile.

The temperatures of A, B, and C were read by means of thermocouples inserted into their edges. The whole pile was varnished so that its emissivity was the same throughout.

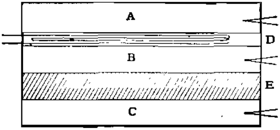

Fig. 106

The total heat supplied was calculated from the current in the coil and its resistance (Art. 133), and as all this heat was emitted from the surface of the pile, the rate at which heat was leaving the surfaces of each of the plates was known. Thus the quantities of heat flowing into the top of E and out at the bottom of E were known, and the mean of these quantities was taken as the quantity H in the formula of Art. 140.

The variation in the conductivity in different directions possessed by æolotropic substances such as crystals was demonstrated by de Senarmont by an arrangement illustrated in fig. 107, where AB represents a thin lamina of the crystal, CDE a silver tube passing normally through AB, F a lamp, and G a screen. The lamina AB was covered with a thin coating of beeswax, and when the tube CDE was heated by the lamp, the wax melted round the hole H.

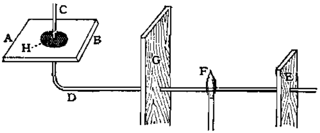

Fig. 107

He found that the shape of the melted area varied according to the direction in which it was cut with reference to the crystallographic axes. The area was circular in isotropic substances and therefore in cubic crystals, and also in crystals of other forms when the material was optically symmetrical with regard to the normal to the lamina. In other cases the area was an ellipse or some form of oval. If heat be supplied to a point in a crystal, the isothermic surfaces enclosing the point are ellipsoids whose axes coincide with the axes of the crystal.

149. CONDUCTIVITY OF LIQUIDS.—All liquids, except metals, are bad conductors of heat. Water may easily be boiled at the top of a tube while the bottom contains a mass of ice. It is not easy to eliminate convection currents in experiments on the conductivity of fluids. This fact, together with the difficulties introduced by the containing vessel and the smallness of the effect to be observed, make many of the results so far attained of doubtful value. We proceed to indicate the methods that have been adopted.

Despretz filled with water a tall wooden cylinder A (fig. 108), and arranged a number of thermometers horizontally with their bulbs on the axis of the cylinder and their stems outside. Fitting into the top of A was a copper cylinder B, which was kept full of hot water that entered by a tube C and left by a tube D. The apparatus was allowed to stand for about thirty-six hours in order that the stationary condition might be attained, and it was then found that the curve of temperature given by the thermometers was the same as that given by a metal bar following the law of Fourier (Art. 140), viz. as the distances from the source of heat increased in arithmetical progression the excess of temperature decreased in geometric progression.

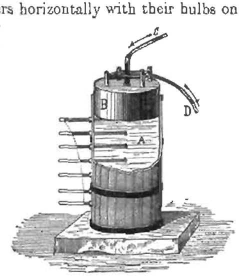

Fig. 108

Weber's latest arrangement was very similar to that of Despretz. The liquid was contained in a vessel having glass sides and a copper base, and standing on a block of ice. In contact with the top of the liquid was a metal vessel containing liquid paraffin, which was maintained at a definite temperature by an electric current passing round a coil of wire immersed in it. The amount of heat supplied was ascertained by the method of Art. 133. Two thermo-electric couples of constantan and iron placed in the liquid one vertically under the other, at a distance apart of 1 cm., measured the temperature difference between the two faces of a layer of that thickness.

Berget has made some experiments by the guard-ring method, employing a Bunsen's calorimeter to measure the quantity of heat transmitted. In the case of mercury the tube AB (fig. 109) was

filled, and surrounded by a cylinder CD also filled with mercury, and standing on an iron plate that formed the top of a chamber in which the lower part of the calorimeter was immersed. This chamber was filled with ice. The upper surface of the mercury was heated by a current of steam. As the mercury in the jacketing cylinder had the same temperature gradient as that in the tube AB, there was no lateral flow of heat. This gradient was measured by a series of iron wires inserted at various depths in the tube AB, which made with the mercury, thermo-couples. The quantity of heat transmitted down AB was known from the indications of the mercury in the tube E, which showed the quantity of ice melted.

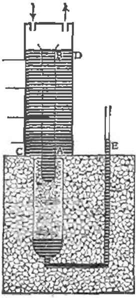

Fig. 100

In some valuable measurements made by Lees, the liquid was contained in a thin cylindrical hollow cut from a plate of ebonite RR (fig. 110), the bottom and top being closed by copper plates A and B. On B were placed successively a plate of glass C of known conductivity, a plate of copper D, a coil of wire Z, and a plate of copper E. The heat was supplied by a current of electricity passing round the coil Z, and was accurately known. The temperatures of the three copper plates D, B, A were determined by thermo-couples inserted in them. The whole pile of plates was varnished, and the emissivity of the surface being known, the amount of heat lost from the surface of each of the plates was known. The amount of heat leaving the lower surface of B was the difference between the quantity generated in Z and the quantity radiated from the surfaces D, C, B, E. Also, the quantity of heat that reached A was known from the quantity emitted by its surface.

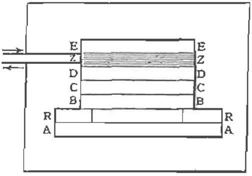

Fig. 110

Two experiments, one with the hollow cylinder empty and one with it filled with liquid, gave the quantity H of Art. 140, the tem-

peratures of the two faces being given by the thermo-couples in B and A. Hence the conductivity of the liquid could be calculated.

The values recently obtained for the conductivity of water range from ·00131 to ·00143, glycerine ·00066 to ·00068, methyl-alcohol ·00048 to ·00049, and mercury ·0197 to ·0201.

150. CONDUCTIVITY OF GASES.—The experimental difficulties in these investigations are great, owing to the effects of convection currents and of radiation. The method generally adopted is to observe the rate of cooling of some hot body placed within the gas.

Kundt and Warburg observed the rate of cooling of a thermometer of approximately known heat capacity in an enclosure of which the outer walls were kept at 0° C. They found that when the gas in the enclosure was at any pressure less than 150 mm. of mercury the thermometer always cooled at the same rate, and they concluded that at such low pressures the effects of convection currents were negligibly small. Moreover, theoretical considerations indicate that the conductivity itself of a gas, within limits, does not vary with the pressure, and therefore the conductivity may fairly be measured at low pressures. They then proceeded to observe the rate of cooling of the thermometer when the enclosure containing it was as perfect a vacuum as could be obtained (under which circumstances it cooled mainly by radiation); and then admitting gas into the enclosure at low pressure, the rate of cooling was again observed. The difference between these observations gave the quantity of heat conducted from the thermometer to the walls of the enclosure by the gas. The calculation is the same as that of Art. 140.

They made observations with various gases and at various (low) pressures. The heat capacity of their thermometer was not very accurately known, but they found for air, k = ·000048, and for hydrogen, k = ·000341.

Employing the same method, and taking into account the effect due to the mercury vapour present from the manometer, Müller has obtained for air, k = ·000056. Maxwell's calculated value was ·000055.

Stefan used an air thermometer with a cylindrical reservoir, which he surrounded with a large concentric cylinder, the gas to be experimented on occupying the space between. The value obtained for the conductivity of air in C.G.S. measure was ·000056.

Recent determinations for air at − 150° C. gave the value k = ·0000215.

151. EXAMPLES.

1. If the conductivity of sandstone be ·0027 C.G.S. units, and if the underground temperature in a sandstone district increases 1° C. for 27 m. descent, calculate the heat lost per hour by a square kilometre of the earth's surface in that district.

Conductivity of sandstone = ·0027 C.G.S. unit. This means that if we have a cubic centimetre of sandstone with its opposite faces differing by 1° C., then ·0027 calorie pass through it per second.

∴ through	1 sq. m.	of area,	1 cm.	thick,	10000 × ·0027	calories	pass	per second.
,,	1	,,	,,	1 m.	,,	27 ÷ 100	,,	,,	,,
,,	1	,,	,,	27 m.	,,	$\frac{1}{100}$	,,	,,	,,
,,	1	,,	,,	27 m.	,,	36	,,	,,	per hour.
,,	1 sq. Km.	,,		27 m.	,,	36×10^6	,,	,,	,,

Ans. 36×10^6 calories.

2. An approximate measurement of the conductivity of certain substances may be made by the method illustrated in the following example: A steady stream of water flowing at the rate of 500 grm. per minute through a glass tube 30 cm. long, 1 cm. in external diameter, and 8 mm. in bore, the outside of which is surrounded by steam at 100° C., is raised in temperature from 20° C. to 30° C. as it passes through the tube. Find approximately the conductivity of the glass.

In the formula, $H = kA\frac{\tau_1 - \tau_2}{l}t$.

$$H = 500(30 - 20) = 5000 \text{ calories,}$$

taking A as the mean of the inner and outer surfaces of the glass;

$$A = 2\pi(\cdot 45) \times 30 = 27\pi \text{ sq. cm.,}$$

taking the temperature difference at the middle of the length of the tube;

$$\tau_1 - \tau_2 = 100 - \tfrac{1}{2}(30 + 20) = 75°;$$

$$l = \text{thickness of the glass} = \cdot 1 \text{ cm.};$$

$$t = 60.$$

$$\therefore 5000 = k \times 27\pi \times 75 \times 10 \times 60.$$

$$\therefore k = \frac{1}{243\pi} = \cdot 0013.$$

An accurate solution of the problem can only be obtained by mathematical methods too advanced for this book.

3. How many kilogrammes of water will be evaporated in 1 hour from an iron boiler 1·5 cm. thick with an area of heating surface equal to 460 sq. cm., the outer surface being kept at 180° C. and the water at 100° C.? The specific thermal conductivity of iron = ·175 C.G.S. unit, and the latent heat of steam at 100° = 540.

$$H = kA\frac{\tau_1 - \tau_2}{l}t.$$

Here $k = \cdot 175$; $A = 460$; $\tau_1 - \tau_2 = 80$; $l = 1\cdot 5$; $t = 3600$;

$$\therefore H = \tfrac{7}{40} \times \tfrac{460}{1} \times \tfrac{2}{3} \times 80 \times 3600$$

$$= 15456000 \text{ calories.}$$

To evaporate 1 kg. of water requires 540000 calories.

Therefore mass evaporated $= \frac{15456000}{540000} = 28\cdot 6$ kg.

QUESTIONS AND EXERCISES

1. When very short cylinders of lead and copper are placed with one end of each in contact with a hot body it is found that the other end of the lead cylinder gets hot soonest, whereas with longer cylinders of the same metals the reverse appears to be the case. Explain the reason of this.
2. How may the conductivity of a substance for heat be measured (*a*) for a metal, (*b*) for a poor conductor?
3. What experiments are necessary to determine the relation between the thermal conductivity of a body and its temperature?
4. Water kept at 15° C. is separated from ice by a plate of iron 1 cm. thick and 100 sq. cm. in area. If 11840 grm. of ice are melted in 1 hour, what is the thermal conductivity of the iron? [Latent heat of water = 80 units.]
5. How may the thermal conductivity of a gas be ascertained?
6. An iron boiler containing water at 100° C. is 3 cm. thick, and keeps a room in which it is placed at a temperature of 30° C. If the conductivity of iron is 1·29 unit per hour, find how much heat is given off per hour from a square centimetre of the surface.
7. How many gramme degrees of heat will be conducted in a second through an iron bar 4 sq. cm. in section, and 2 cm. long, one end being kept at 178° C. and the other at 100° C., the mean conductivity of iron being ·12? [Units: gramme, centimetre, second, degree C°.]
8. Boiling water is kept in contact with a brass plate 1 cm. thick and 100 sq. cm. in area; the other side of the plate is in contact with melting ice and it is found that 64·92 kg. of ice are melted in 24 min. Find the specific thermal conductivity of brass in C.G.S. units. [L = 80.]
9. Compare the quantities of heat which pass through two plates of the same material from the following data:—

	Time.	Area.	Thickness.	Temperature Difference of Faces.
Plate A ...	1 hour.	20 sq. ft.	12 in.	1° C.
Plate B ...	15 min.	14 sq. ft.	·5 in.	20° C.

10. The bottom of an iron saucepan has an area of 150 sq. cm. and a thickness of ·3 cm. Supposing it to stand on a hot plate maintained at a temperature of 150° C. while the saucepan contains water at 100°, find how much water would be evaporated per minute. [Thermal conductivity of iron, ·16.]

CHAPTER XV

THERMO-CHEMISTRY

152. HEAT OF COMBINATION.—The ordinary method of producing heat is by chemical combination. When substances chemically combine—e.g. hydrogen and oxygen to form water—heat is evolved, and when water is decomposed into its constituent gases energy is absorbed. If the direct and inverse process take place under the same external conditions these two quantities of energy are equal.

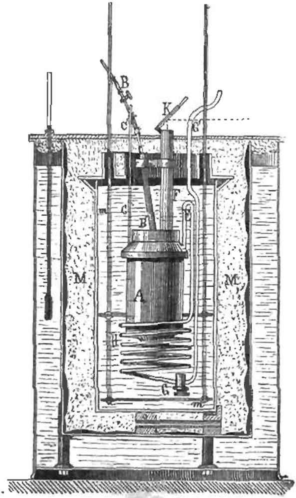

Fig. 111

We shall confine our attention to a few of the more simple and common of such combinations.

The **heat of combination** *of a substance A with another substance is the quantity of heat evolved when unit mass of A combines chemically with the second substance.* The quantity of the second substance that enters into the compound is determined by the nature of the compound formed. In all measurements of the heat of combination, known weights of the substance are caused to combine in a calorimeter, and the heat produced is measured by the rise of temperature of the surrounding liquid, which is generally water or mercury.

153. EXPERIMENTS OF FAVRE AND SILBERMANN.—These investigators made numerous and accurate observations on the heat produced when different substances were burned in oxygen. Their calorimeter is shown in fig. 111.

The substances were burned in the chamber A, which was made of copper and wholly immersed in the water of the calorimeter M. The calorimeter was surrounded by a water jacket, and the space between these vessels was filled with swans' down.

The vessel A was kept full of oxygen by means of the tube CC', which communicated with a large reservoir of that gas. When the substance burned was a gas it passed into the calorimeter in a steady stream through the tube BB'. When the substance was solid or liquid this tube was utilized for the purpose of directing a jet of oxygen upon the burning mass. Liquids were burned in a lamp with an asbestos wick.

The products of the combustion were cooled in passing through the coil H, after which they either condensed in the reservoir G or passed into the air through the tube G'.

A tube K closed by a glass window enabled the process to be watched in order that the combustion might be regulated.

The temperature of the calorimeter was carefully corrected for radiation according to Newton's law of cooling.

By the same method Favre and Silbermann also measured the heat developed when various substances were burned in chlorine.

154. ANDREWS' EXPERIMENTS.—The apparatus used by Andrews to determine the heat evolved in the combination of two gases is shown in fig. 112. The gases were introduced into a vessel a, which was made of thin sheet copper and placed inside a larger vessel containing water. The calorimeter thus formed was placed in a cylinder mounted on a horizontal axis, and when by rotation of the apparatus the gases and water had been caused to take up a common temperature this temperature was carefully read on a delicate thermometer Through the vessel a passed a fine platinum wire, and the gases were caused to explode by heating this wire to a white heat by means of an electric current. The apparatus was then again rotated for several seconds to agitate the water, and its temperature was again read.

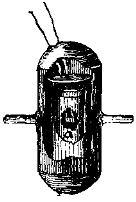

Fig. 112

155. The heat developed in chemical combinations which do not produce combustion was measured by Favre and Silbermann by means of the apparatus shown in fig. 113. An iron reservoir R, filled with mercury, contained at its centre a chamber in which the

chemical action took place. The heat produced caused the mercury to expand along a communicating tube ll', and the quantity of heat was calculated from the amount of this expansion. The materials were introduced into the calorimeter R through a tube m, the solid substance being first introduced, and the liquid subsequently by inverting the bent tube B. A plunger turned by the handle M served at the beginning of every experiment to set the mercury at the zero point O in the tube. The relation between the expansion of the mercury in ll' and the heat developed in R was independently determined by placing in R a known weight of water and

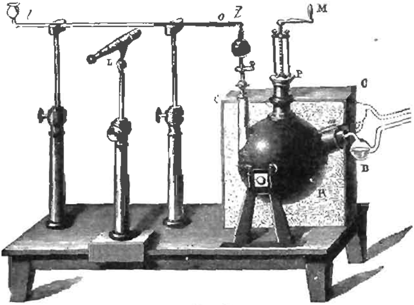

Fig. 113

observing the advance along ll' for the known number of calories thus communicated. The calorimeter was surrounded by wool to prevent loss of heat by radiation.

The results obtained for a few substances are given in the table on page 415.

156. The **calorific value** of fuel is determined by burning a small mass and passing the gaseous products of combustion through water, the heating of which measures the quantity of heat evolved.

Fig. 114 shows a modified form of the Thomson calorimeter. The combustion takes place inside the vessel A, which stands in a known mass of water contained in a larger vessel C. When in action the vessel A is closed at top and bottom. The fuel contained

in a crucible inside A is ignited by an electric current passing through a wire, and the combustion is maintained by a stream of oxygen passed into A. The necessary accessories are shown at B. The heated gases pass out through a valve at the bottom of A and bubble up through the water in C, the rise of temperature of the water being measured by a delicate thermometer D. To check radiation the calorimeter C is placed inside a metal vessel E, which stands in a box of wood F. It is necessary that the water-equivalent of the

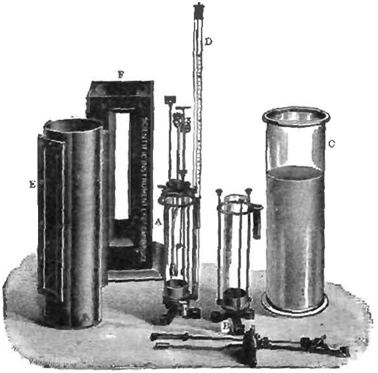

Fig. 114

apparatus should be known and added to the actual mass of water used.

157. The temperature attained during combustion varies with the materials and the velocity of the chemical change. Ignition temperature is the temperature to which a body must be raised in order that combustion may begin. Flames are gases that are heated sufficiently to become self-luminous, but some flames that are very hot give little light owing to the lack of solid particles in the flame. If a flame be cooled by any means below the temperature at which rapid chemical action takes place, the flame is extinguished.

Attempts have been made to calculate the temperature of flame by finding the quantity of heat developed and dividing it by the heat capacity of the products. Thus 1 lb. of carbon in burning gives out 8000 units (pound-degrees) of heat. If burned in air the gaseous products weigh about 12·5 lb. Taking the specific heat of these products as ·24, the number of heat units required to raise them through 1° C. = 12·5 × ·24 = 3, whence the temperature reached = 8000 ÷ 3 = 2666° C. Objections to the method are obvious, and such results are not to be relied on.

158. EXAMPLES.

1. How many pounds of water could be evaporated by the heat developed by the combustion of 1 lb. of hydrogen in oxygen?

The combustion of 1 lb. of hydrogen in oxygen produces 34000 pound-degrees of heat.

The evaporation of 1 lb. of water absorbs 537 pound-degrees.

$$\therefore \text{ Mass evaporated } = \frac{34000}{537} = 63{\cdot}3 \text{ lb.}$$

2. How many grammes of carbon must be completely burned to produce heat enough to convert 10 grm. of ice at −5° C. into steam at 100° C.?

[Heat of combustion of carbon 8088 units; latent heat of water 79 and of steam 536; specific heat of ice ·5.]

To warm	10 grm. of ice from −5° C. to 0° C. absorbs		25	calories.
To melt	10 ,, ,, at 0°	,,	790	,,
To warm	10 ,, water from 0° C. to 100° C.	,,	1000	,,
To evaporate	10 ,, ,, at 100°	,,	5360	,,
	∴ Total heat required =		7175	,,

$$\therefore \text{ Carbon required } = \frac{7175}{8088} = {\cdot}887 \text{ grm.}$$

QUESTIONS AND EXERCISES

1. The heat of combustion of zinc in oxygen is said to be 1300. Explain what this statement means, and describe the apparatus and experiments by which it may be verified.
2. How would you find experimentally the relative quantities of heat given off when equal weights of sulphur, phosphorus, and carbon are thoroughly burned?
3. Why do the inhabitants of cold climates eat fat?
4. How much charcoal must be burned per hour inside a cube to maintain the temperature of the inside 20° hotter than the outside, if the edge of the cube be 5 m., the thickness of the walls 10 cm., and the conductivity of the material ·0056 C.G.S. unit?
5. How much ice at 0° C. would be converted into steam at 100° C. by the combustion of 1 grm. of hydrogen?
6. How much iron must be burned to produce sufficient heat to warm a ton of iron from 15° C. to 25° C.?

CHAPTER XVI

RADIATION

159. NATURE OF RADIATION.—The modes by which heat may pass from one body to another have been distinguished in Chap. I. Ordinary material substances are concerned in the processes of convection and conduction; but in radiation the passage takes place by means of the *ether*. A mass of evidence, which appears mainly in the theory of light and electricity, suggests the existence of this universal medium, which fills all "empty" space, whether between stellar systems or between molecules. It is a unique substance, apparently possessing properties not usually combined in the substances we know. For example, astronomy postulates its possession of the properties of a perfect fluid, while the facts of physics seem to show that it possesses the properties of an elastic solid, having a considerable density, but is apparently not subject to the law of gravitation.

All processes such as gravitation and radiation, which used to be vaguely described as "action at a distance", are now considered to be due to continuous forces acting through the ether.

The process of radiation is supposed to be something of the following nature. The particles of a hot body are in a state of rapid vibration; these vibrations communicate themselves to the ether which surrounds them; undulations are thus formed in the ether which travel out in all directions, and when impinging on matter set in rhythmical motion those particles whose natural rate of vibration is of the same frequency as the undulations which fall on them. The process is something like that which takes place when we give a jerk to one end of a heavy cord, causing a wave to run along the cord, which results in a jerk at the other end, the motion of the parts of the medium being at right angles to the direction of propagation of the wave.

A hot body, such as the sun or a flame, emits undulations of various wave lengths. The radiation from a cooler body, such as a vessel of hot water, consists chiefly of the longer wave lengths, the energy of the shorter waves emitted by the hotter body being negligible. Hence experimental differences are found depending for their explanation on the temperature of the source of radiation employed (Art. 172).

In order to explain certain phenomena in light, e.g. refraction, Fresnel considered that the properties of ether were modified by its

entanglement among the particles of ordinary matter, that it was denser when thus entangled or "bound", than when "free" in space, and was thus modified more or less in its capacity for carrying undulations. Hence different bodies behave in different ways with regard to the transmission of radiation.

The consideration of radiation generally is usually given in books on Light or on Radiant Energy. It is a very large subject, of which we can only give a small portion connected more closely with Heat proper. Radiant energy proceeding from a body is generally called radiation, and not radiant heat, because during the time of its existence in space it is not in the form of heat, as it exists in ordinary matter.

160. RADIOMETERS.—For the quantitative investigation of radiation various means are employed.

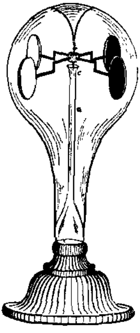

Fig. 115

Crookes' radiometer consists of a vacuous chamber in the form of a pear-shaped glass bulb, within which is delicately suspended a system of vertical vanes. The disks of the vanes are made of pith or of aluminium, coated with lampblack on one side, and are fixed at the ends of two arms (fig. 115) at right angles to each other in such a manner that, as they rotate, the blackened sides all face the same way. The arms, made of thin glass or some light material, are fixed to a centre piece *b* of pith, which is supported on a very fine needle point resting in a glass cup *c* at the top of the glass tube *a*.

When this instrument is exposed to a source of radiation, the vanes revolve with a speed which indicates the intensity of the incident radiation.

The origin of the motion is the impact of the gaseous particles (Art. 224) on the surfaces of the vanes. Lampblack being a much more powerful absorbent than metal or pith, the former surface becomes a little warmer than the latter. The particles that impinge on the lampblack surface there receive an additional quantity of energy of motion, and rebound with a greater velocity than those which impinge on the metallic surface. The greater energy of the rebound produces a resultant pressure on the lampblack surface, and

therefore causes it to start moving in the opposite direction to the normal component of the motion of the molecules.

After a short period, however, when the rebounding molecules of the gas have shared their energy with the adjacent molecules, this cause ceases to operate over the central portion of the vane, *but continues to do so round the edges sufficiently to maintain the* motion. By placing a quantity of cold powdered charcoal in communication with the chamber of the radiometer, Dewar has succeeded in making the vacuum so perfect that the vanes no longer rotate.

For some of his experiments on radiation, Nichols modified the instrument so as to convert it into a measuring instrument. There were two vanes suspended by a delicate quartz fibre. One vane was screened from the radiation which fell on the other, and the torsion of the suspending fibre caused a definite deflection to take the place of rotation. The angle of deflection was shown by a mirror attached to the suspended system as in the mirror galvanometer. This form of the instrument is very sensitive, and allows comparative measurements to be made.

The Linear Thermopile.—The extreme sensitiveness of some modern galvanometers renders it practicable to work with a thermopile having very few pairs, or even only one pair, of bars. The *linear thermopile* is sometimes used in the examination of the spectrum. The couples are made of fine wire, iron and constantan being often used. The wires are wound on a small frame, every alternate junction lying on a vertical line, and the frame is placed in a cylinder which has a small vertical slit in it through which radiation passes to the line of junctions.

Boy's Radio-micrometer (fig. 116) is a combination of a thermocouple and a delicate galvanometer. The bar of bismuth and the bar of antimony are joined at their lower extremities to a thin copper disk *d* and at their upper extremities to a single loop of fine bare copper wire *c*, the whole thus forming an electric circuit. The loop of copper wire is supported by a thin glass tube *g*, and this in turn by a fine quartz fibre *q*. The glass tube carries the galvanometer mirror *m*. All these arrangements are suspended within a brass tube (shown shaded), which throughout the length of the coil of copper wire is between the poles of a powerful permanent magnet NS, and the bismuth-antimony couple is surrounded by a mass of soft iron AA. The radiation enters through the tube B, falls on the disk *d*, and thus warms the lower junction of the thermo-couple and causes an electric current to flow round the coil *c* (Art. 135), which

being in a strong magnetic field and only lightly controlled by the quartz suspension, is easily deflected. The deflection is shown by a beam of light reflected from the mirror *m*. The instrument is quick in action, very delicate, and has a constant zero due to the perfect elasticity of the quartz fibre suspension.

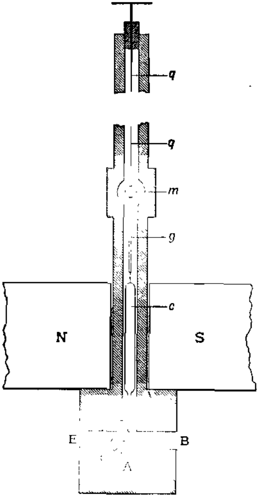

Fig. 116

The Bolometer.—One of the most sensitive instruments in use for the measurement of thermal radiation is the bolometer, invented by Langley when making his researches on Mount Whitney in America. It consists essentially of a series of thin strips of steel, platinum, or palladium about 1 cm. long, less than 1 mm. wide, and $\frac{1}{250}$ mm. ($\frac{1}{6250}$ in.) thick, arranged as in fig. 117 so as to form a continuous flat wire.

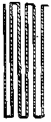
Fig. 117

Two such exactly similar wires form the adjacent arms of a Wheatstone's bridge connected with a strong battery and a delicate galvanometer. The electrical resistance of the bolometer wire is very high owing to the smallness of its section, while its large surface and small thickness render it very susceptible to change of temperature.

When, therefore, one bolometer wire is exposed to some source of radiation from which the other is shielded, the exposed wire becomes warmer, its electrical resistance increases (Art. 134), and the disturbance of the balance of the Wheatstone's bridge is indicated by a deflection of the galvanometer.

The instrument is sufficiently sensitive to allow of the measure-

ment of ·0001° C., and the action is more prompt than that of the thermopile. Hence it is much used in investigations of the thermal spectrum.

161. RADIANT HEAT AND LIGHT COMPARED.—

Radiation through a Vacuum.—Heat and light are received simultaneously from the sun, and when the light is cut off at the time of an eclipse, the heat supply also ceases. Thus thermal radiation is transmitted through vacuous space at the same speed as light radiation.

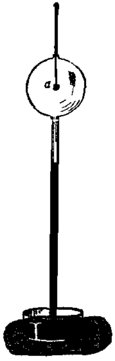

Fig. 118

That thermal radiation which is unaccompanied by light radiation may also pass through a vacuum is shown by the following experiment devised by Rumford. The closed end of a barometer tube was expanded into a sphere (fig. 118), at the centre of which was placed the bulb of a thermometer. The barometer tube was then filled with mercury, and a vacuum produced at the top as with an ordinary barometer. On allowing thermal radiation to fall on the sphere the thermometer showed a rise of temperature, just as in the case when the sphere was filled with air. Thus thermal radiation does not need the presence of air or other ponderable medium for its transmission.

Radiation travels in Straight Lines.—If a radiometer be exposed to a source that is emitting both thermal and light radiation, it is found that when the light radiation is stopped by a series of screens the radiometer is also unaffected; if the screens be pierced so that light passes through them. a radiometer in the path of the ray shows a deflection. And the radiometer gives the same kind of indication when the source of radiation is hot but dark. Thus thermal radiation, like light radiation, travels in a straight line from the source; we have thermal shadows precisely like light shadows; and we may speak of and treat of rays and pencils and beams of thermal radiation in the same manner as geometrical optics treats of light.

Law of Inverse Squares.—The important law that the intensity of the radiation proceeding from any given source varies inversely as the square of the distance from the source, may be experimentally proved by means of the apparatus shown in fig. 119.

The source of radiation is a vessel containing hot water, having

one of its faces AB plane and coated with lampblack. A thermopile (Art. 136), shielded from lateral effects by a cone fitted on to one face, is placed at various distances S and S′ from the radiating surface, and the indications of the galvanometer are found to be constant whatever the size of the circular area AB from which the radiation proceeds. The area of this circle is proportional to the square of the distance between it and the thermo-pile. The intensity

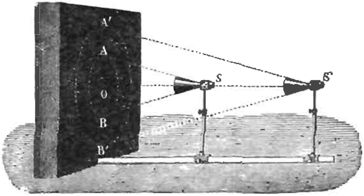

Fig. 119

of the radiation received by the thermo-pile from any definite area is therefore inversely as the square of that distance.

Reflection.—The fact that thermal radiations undergo regular reflection under proper conditions may be proved by the following experiments.

If a concave mirror be placed with its axis directed towards the sun, a thermometer placed at its focus at once indicates a rise of temperature. Metals have been melted in this way.

If two parabolic mirrors be placed some distance apart, with their concave surfaces facing each other and their axes in the same straight line, and a hot body be placed in the focus of one mirror, the radiations from this source after reflection from the mirror converge to the focus of the second mirror and raise the temperature of a substance placed there (fig. 120). If the source of heat be luminous, an image both luminous and hot is obtained in the focus of the second mirror. The thermal and luminous radiations have followed the same paths. If the source of heat be a dark vessel containing a hot liquid, a thermometer placed in the other focus shows a rise of temperature. Thus thermal radiation falling on polished surfaces is reflected according to the laws of reflection of light. The laws are:—

(1) The incident and reflected rays are in the same plane.
(2) The angle of reflection is equal to the angle of incidence.

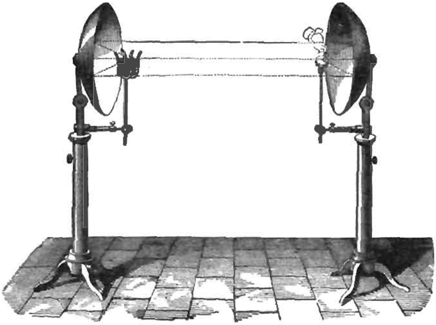

Fig. 120

Polarization.—It has long been known that light radiation which has been transmitted through a plate of tourmaline is *quenched by a similar plate of tourmaline placed in the path of the* rays in a certain position, and is transmitted by the second plate when placed *in another position*. The explanation of this phenomenon is as follows. The ether vibrations which are incident on the first plate take place in all planes that pass through the line of propagation of the wave, while the plate transmits only those vibrations which are taking place in one plane, quenching all the rest. Light radiation of which the vibrations are taking place in one plane only, is said to be **polarized**. When the light that has been polarized by its passage through the first plate falls on the second plate, it is either quenched or transmitted according to the relation which the plane of vibration of the light bears to the optic axis of the crystal.

Light radiation may be polarized in various ways, such as by reflection from blackened glass or from a pile of thin plates of various materials.

If a radiometer or one of the more delicate instruments for

detecting thermal radiation replace the eye in these experiments, it shows that the thermal radiations are transmitted or quenched in precisely the same way as the light radiation, not only when the source of radiation is emitting both light and thermal radiations simultaneously, but also when the source is at such a temperature as to emit thermal radiations only.

Heat radiation is thus shown to be capable of polarization in precisely the same way and by the same means as is light radiation.

The **refraction** of thermal radiations is dealt with in Art. 176.

162. In the succeeding articles we shall give a sketch of the earlier work on the behaviour of bodies with regard to thermal radiation, and for these purposes the subject may be thus divided.

A. Radiation proceeding from a given substance. This process is called **emission**.

B. Radiation incident upon a given substance.

When radiation is incident upon any given substance, the radiation either enters the substance or is reflected from the surface.

If it is reflected, the reflection may be either regular or irregular. **Regular reflection**, or simply **reflection**, is the case when the radiation proceeds in the same manner as the reflection of light from a mirror, the reflected pencil taking a definite direction. Irregular reflection or **diffusion** occurs when the radiation is reflected in all directions, as the light is from this page.

If the radiation enters the substance, it may or may not pass through it. That which passes through is said to undergo **transmission**; that which enters the substance but does not pass through it, is said to undergo **absorption**.

Thus

Incident Radiation	either enters a substance	and passes through	—Transmission.
		or is quenched	—Absorption.
	or undergoes reflection	regularly	—Reflection.
		or irregularly	—Diffusion.

When a body transmits thermal radiation, its temperature is of course unaffected by that which it transmits; its temperature is raised only by that which it absorbs.

The relation between the quantities of radiation that are transmitted, absorbed, reflected, or diffused, may be thus shown. Suppose unit quantity of radiant energy to fall upon a substance

of which a certain fraction $\frac{1}{n}$ is transmitted, $\frac{1}{a}$ is absorbed, $\frac{1}{r}$ reflected, and $\frac{1}{d}$ diffused, then

$$\frac{1}{n} + \frac{1}{a} + \frac{1}{r} + \frac{1}{d} = 1.$$

These fractions are respectively the measures of the transmitting, absorbing, reflecting, and diffusive powers of the substance.

If, as is the case at least approximately with many substances, $\frac{1}{n} = 0$, that is, the substance does not transmit some particular kind of radiation, then the sum of the three remaining fractions equals unity.

163. THEORY OF EXCHANGES.—If we have a mass of white-hot platinum, and a vessel containing water at 100°, we know that each source is emitting radiation in all directions, so that radiation from each must fall upon the other if there is no obstacle between them.

If the hand be held in front of one face of a thermopile, the galvanometer is at once deflected, and if the hand be replaced by a lump of ice, a deflection is obtained in the opposite direction, showing an apparent radiation of cold.

Such facts suggested to Prévost the idea that radiation is taking place from all bodies whatever their temperature may be, and that every body is continually emitting aud receiving radiations from others. No bodies are absolutely devoid of heat, and their molecules are always in motion. They are continuously producing undulations in the ether, i.e. emitting radiation, and also taking up the suitable undulations that fall on them, i.e. absorbing radiation, thus exchanging radiation with all bodies near them whether hot or cold.

164. EMISSION.—The total loss of heat from any given hot body depends upon several circumstances. It, of course, varies with the time considered; and when it takes place *in vacuo*, the rate is found also to depend upon the nature, form, extent, and condition of the surface, upon the mass of the radiating body, and upon the temperature of the body itself and of surrounding bodies.

When cooling takes place in any gas, the rate is further affected by the conductivity of the gas and by the convection current formed, so that we are not dealing with radiation only.

165. NATURE OF THE SURFACE.—The nature of the sur

face has an important effect on the rate at which heat leaves a body. If we take two similar flasks, cover one with lampblack and the other with tinfoil, fill them both with hot water and observe the rate at which they cool, it is found that the flask covered with lampblack cools much the faster of the two. Hot water, contained in a vessel with a polished surface, keeps hot longer than in a similar vessel with a rough dull surface. Placing a polished vessel in a tight-fitting coat of thin flannel hastens rather than retards the cooling, the increased emissive power of the surface more than compensating for the effect of the bad conductivity of the flannel.

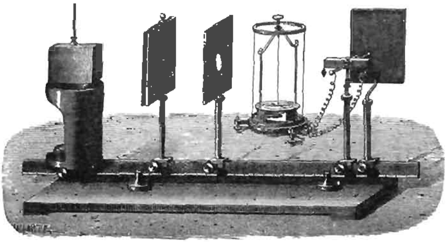

Fig. 121

The earliest comparisons of the loss of heat of different substances under the same conditions were made by Leslie. He took a hollow cube of thin metal containing hot water, and having each of its sides covered with different material, and placed it before a concave mirror, at the focus of which was a differential thermometer. Although the faces of the cube were all at the same temperature, the rise of temperature registered by the thermometer varied according to the nature of the material on that face of the cube from which it was heated.

More exact measurements were afterwards made by Melloni, by means of the apparatus shown in fig. 121. A Leslie's cube, having its faces coated with different substances, was filled with water maintained at boiling-point by a lamp, and the radiation from the different faces was successively received on one face of a thermopile attached to a galvanometer. The current recorded by the galvanometer was

proportional to the heat absorbed by the thermopile, i.e. to the heat radiated from the face of the cube, which was determined by the *emissive power of the substance with which it was coated.*

A pierced screen served to limit the area from which heat rays passed to the thermopile, and another movable screen to commence and terminate the experiment.

De la Provostaye and Desains found that the pierced screen used by Melloni reflected rays back to the cube, from whence they were again reflected so as to reach the thermopile. They therefore blackened this screen on the side of the cube, and polished it on the side of the pile, and interposed a second similar screen to prevent radiation to the pile from the first screen. By this means they eliminated the errors which vitiated Melloni's results for metals.

By using screens pierced with apertures of different sizes, the apparatus could be made more or less sensitive in a known ratio at pleasure.

In the final resnlts it was found that lampblack has the highest, and polished metals have the lowest emissive power.

TABLE OF COMPARATIVE EMISSIVE POWERS

(Melloni.)		(De la Provostaye and Desains.)	
Lampblack	100	Platinum (polished) ...	9·5
White lead	100	Copper foil	4·9
Paper	98	Gold leaf	4·3
Glass	90	Silver	2·2 to 5·4
Indian ink	85	(according to state of polish).	
Shellac	72		

The above measurements are comparative. Few data are available as to the absolute emissive power of substances.

166. The **emissivity**, emissive power, or coefficient of emission of a body, is the quantity of heat radiated per second from unit area of surface per degree of difference between the temperature of the substance and that of the enclosure.

M'Farlane, in his determinations, hung a small blackened copper sphere inside a calorimeter the inside of which was also blackened, and which had double walls, the interspace being filled with water. The sphere was first heated in a flame and then hung in position. One junction of a thermo-couple was embedded at the centre of the sphere and the other fixed to the outside of the calorimeter. The deflections of the galvanometer included in the circuit were read at suitable intervals during the cooling of the sphere. *The thermo-*

couple having been standardized, the temperature of the sphere at any moment was known from these deflections.

He also made a set of observations when the surfaces were bright. The following values of the emissivity were obtained:—

Surface.	Temp. of Enclosure.	Temperature Difference.	Coefficient.
Polished copper ...	14° C.	5° C.	·000188
" " ...	14°	60°	·000226
Blackened copper ...	14°	5°	·000252
" " ...	14°	60°	·000328

The presence of air largely affects the results. Art. 150.

In some experiments by Bottomley a platinum wire was stretched inside a blackened copper tube, the wire being maintained at a steady temperature by passing an electric current through it, the heat emitted from the surface of the wire being equivalent to the electrical energy supplied (Art. 133). The pressure of the air in the tube was varied in different experiments, and it was found that below a certain pressure further reduction did not affect the results.

The values obtained by him for the emissivity of the platinum were:—

At 408° C. ... ... ·0379
At 505° C. ... ... ·0726

In another series of experiments at low temperatures the same investigator employed a copper globe inside a hollow copper sphere, the space between them being exhausted. He obtained values from ·000096 to ·000056 with different temperatures and excess temperatures.

The emissivity decreases with the temperature. De la Provostaye and Desains, by means of an electric current, heated platinum plates which were coated on the two sides by two different substances. A thermopile was placed opposite each face. Different temperatures were obtained by using weaker or stronger currents. As the temperature was raised both thermopiles produced a greater deflection in their attached galvanometers, but the deflections did not increase in the same ratio. Hence each substance has a special rate of variation of the emissivity with the temperature, i.e. they react differently to waves of different lengths.

167. TEMPERATURE. **Laws of Cooling.**—The rate at which

heat leaves a body also depends upon its excess of temperature above its surroundings. The relation between this rate and the temperature of the body has been the subject of much investigation. As a first approximation *Newton's Law of Cooling* is used in elementary work. The student can easily verify this law. If a mercury thermometer with a large bulb be warmed to a temperature 20° C. or 30° C. above the temperature of the air, suspended in a position free from draughts and observed at convenient eqnal intervals of time, e.g. every minute, it will be found that the rate of cooling is rapid at first and gradually diminishes as the temperature of the thermometer approaches that of the room. It is obvious that in such an experiment we are not dealing with radiation only, but with the total heat that left the thermometer. The numbers expressing the fall of temperature during these successive intervals are proportional to the numbers expressing the differences between the mean temperature of the thermometer during the successive intervals, and that of the enclosure. These facts are embodied in Newton's law of cooling. *The rate of rise or fall of temperature of a body is proportional to the difference between the temperature of the body and that of the enclosure.*

The numbers, which indicate the successive values of the excess of the mean temperature over that of the enclosure, form a geometrical progression proceeding by a common ratio, and the logarithms of these numbers an arithmetical progression proceeding by a common difference. The following actual set of readings will serve to illustrate the law:—

Time	Temperature of Thermometer (*a*).	Temperature of Enclosure (*b*).	Excess of Temperature (*a* − *b*).	Logarithm of Excess of Temperature.	Excess Ratios.
3 hr. 0 min.	95° F.	65° F.	30° F.	1·477	1·24
3 hr. 2 min.	89·1°	65°	24·1°	1·382	1·26
3 hr. 4 min.	84·0°	65°	19°	1·279	1·23
3 hr. 6 min.	80·4°	65°	15·4°	1·187	1·48
3 hr. 10 min.	75·4°	65°	10·4°	1·017	1·51
3 hr. 15 min.	71·9°	65°	6·9°	·838	—

The numbers in the sixth column—"excess ratios"—are obtained by dividing successively each of the numbers in the fourth column by the number next below it. It will be observed that so long as the temperature interval was the same (two minutes) this ratio remained practically constant, and the longer the time interval the greater the ratio.

In the diagram, fig. 122, the observations are plotted. Curve A is the curve of cooling, showing the rate at which the excess of temperature (column 4) varied with the time. Curve B shows the logarithms of the excess of temperature plotted with the time. This line is approximately straight, the divergence of some of the points from the straight line being due to experimental error.

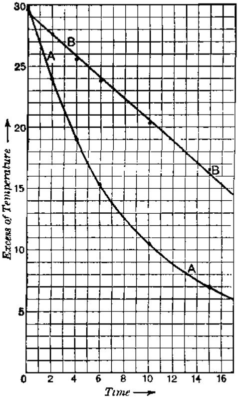

Fig. 122

Example.—A hot iron ball at $T°$ C. is set to cool in an enclosure at 0°. After 5 min. a thermometer is inserted in a hole in the ball; one minute later the temperature is 300° C., and after another minute it is 250° C. Find T.

We may use the diagram, fig. 123.

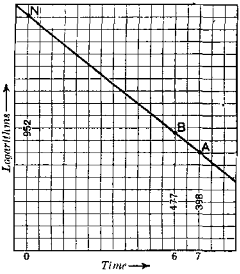

Fig. 123

Omitting the characteristics the logarithms of 250 and 300 are 398 and 477. *Along the axis of time mark off the distances 6 and 7. At these distances set up* ordinates representing on a suitable scale the numbers 477 and 398, thus obtaining the two points AB. Join AB and produce the line to cut the axis of the logarithmic excess at N. Then the length of ON is found to be 952, which is the logarithm of 895: thus 895° C. is the temperature required.

Or we may proceed by calculation thus:—

The temperature at the end of the 6th minute may be obtained by multiplying that at the end of the 7th minute by $\frac{30}{25}$; that at the end of the 5th minute by multiplying that at the end of the 6th minute by the same quantity (1·2); and so on.

Therefore the temperature at the commencement was

$$300° \times (1{\cdot}2)^6 = 300° \times 2{\cdot}984 = 895° \text{ C.}$$

For most practical purposes Newton's law is sufficiently accurate when the temperature difference does not exceed 40° or 50°, but further experiments show that this law does not represent the facts when the difference of temperature between the hot body and the enclosure is considerable, a case which was investigated by Dulong and Petit.

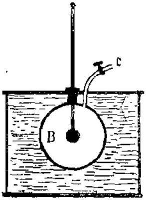

Fig. 124

Dulong and Petit's Law of Cooling.—In their researches Dulong and Petit used as the cooling body a mercury thermometer having a large bulb, the cooling liquid thus registering its own temperature.

The thermometer was placed (fig. 124) with its bulb at the centre of a spherical vessel B of thin copper, about a foot in diameter, coated all over its interior with lampblack. Attached to the top of the sphere was a metal cylinder, through which passed the stem of the thermometer. By means of a tube C air or gas could be pumped in or out of the enclosure B. The sphere B was immersed in a large vessel of water or other substance maintained in each experiment at some definite temperature.

When the enclosure was at 0° Dulong and Petit obtained the following result:—

Temperature of thermometer	240°	200°	160°	120°	100°	80°
Rate of cooling	10·69	7·40	4·89	3·02	2·30	1·74

Thus under these circumstances a thermometer at 240° cools not twice as fast but more than three times as fast as one at 120°, and one at 160° more than two and a half times as fast as one at 80°. The rate of cooling is clearly not proportional to the difference of temperature between the hot body and the enclosure, i.e. Newton's law is not correct when the temperature difference is great.

The theory of exchanges suggests that *the law of cooling is a function not only of the temperature of the hot but also of that of the cold body.*

Dulong and Petit took a series of readings, in which the temperature of the enclosure was maintained at successively higher temperatures, the temperature of the hotter body being always

greater than this by a fixed amount. The following are a few of the readings:—

Temperature of hot body τ_1	100°	120°	140°	160°	180°
Temperature of enclosure τ_2... ...	0°	20°	40°	60°	80°
Rate of cooling	2·3	2·74 $= 2·3(1·16)$	3·16 $= 2·3(1·16)^2$	3·68 $= 2·3(1·16)^3$	4·29 $= 2·3(1·16)^4$

Here we see that the rate of cooling is greater at high than at low temperatures for a given temperature difference between the hot body and its enclosure. In fact, as appears from the fourth line of figures, if the difference $\tau_1 - \tau_2$ be kept constant, then as $\tau_1 + \tau_2$ increases in arithmetical progression the rate of cooling increases in geometrical progression.

The results of Dulong and Petit are embodied in the formula,

$$\text{Rate of cooling} = -\frac{d\tau}{dt} = \mathrm{M}(a^{\tau_1} - a^{\tau_2}),$$

where $\tau = \tau_1 - \tau_2$ and M and a are constants. For Centigrade reading the constant a is 1·0077; M depends upon the nature and mass of the cooling body and the condition of the radiating surfaces, and, according to Dulong and Petit, remains constant for the same pair of surfaces.

The above investigations refer to bodies cooling *in vacuo*. When gas was admitted into the enclosure (fig. 124) Dulong and Petit found that the rate of cooling was increased by an amount different for different gases, and which varied also with the pressure to which the gas was subjected. This effect was due to conduction.

Stefan's Law.—It was pointed out by Stefan that the experimental results of Dulong and Petit may be expressed by the simple law that *the radiating power of a body is proportional to the fourth power of its absolute temperature*, a conclusion which agrees with the theoretical law developed by Boltzmann (Art. 183). This law of cooling may be represented by the formula

$$-\frac{d\theta}{dt} = \mathrm{M}(\theta_1{}^4 - \theta_2{}^4).$$

Some recent researches at very high temperatures have given results differing from Stefan's law, but on the whole the evidence

points to this expression as giving the true law of the variation of radiation with temperature.

168. REFLECTION.—The reflection of thermal radiation from polished surfaces has been investigated by Melloni and by de la Provostaye and Desains by means of the apparatus shown in fig. 125. The reflecting substance was placed on the graduated circular plate D, by turning which the angle of incidence of the pencil of rays could be adjusted to any required value. This pencil proceeded from a Locatelli lamp A, passed through an aperture in the screen C, and after reflection from the plate at D fell upon the thermopile E.

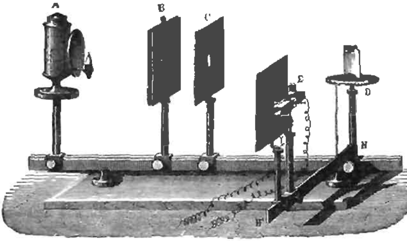

Fig. 125

The deflection of the galvanometer measured the intensity of the radiation falling upon the pile. A movable screen B served to cut off the radiation when required, and another screen served to shield the thermopile from direct radiation from the source of heat. The deflection of the galvanometer was noted: (*a*) when the arrangement was that shown in the figure, and (*b*) when the substance at D was removed and the bar HH' rotated on a pivot at H, so that the thermopile received the direct radiations from the source. The ratio of these readings gave the ratio $\frac{\text{Reflected radiation}}{\text{Incident radiation}}$, which is the measure of the **reflecting power**.

Besides confirming the general conclusion that thermal radiations follow the laws of reflection that apply to light, the experiments indicated:—

(i) For diathermanous substances (Art. 170) the reflecting power

increases with the angle of incidence; whereas for metals it remains nearly constant until the angle reaches 70° or 80°, and then diminishes.

(ii) The reflecting power varies with the source of heat. When the Locatelli lamp was removed and solar radiation used, the value obtained for the reflecting power of silver was smaller.

The reflecting power of a substance is therefore different for incident rays of different wave length.

169. DIFFUSION.—The fact that a part of the thermal radiation incident upon a surface may undergo diffusion is proved by directing thermal radiations upon a substance such as white lead or any white powder and placing the thermopile near it. A deflection is obtained in any position of the pile. The fact that this reflection is due to radiation irregularly reflected from the surface, and not to radiation emitted by the powder itself, is proved by the nature of the radiation, which exhibits the same characteristics as are shown by the radiation from the source. It also appears from Melloni's experiments that when the source of heat is at a high temperature the process of diffusion from any given surface takes place to a greater proportionate extent than when the source of heat is a body of low temperature.

170. TRANSMISSION.—Substances which allow thermal radiations to pass through them are called **diathermanous**, those which will not transmit such radiations are called **athermanous**. Diathermancy for heat is analogous to transparency for light; it is transmissive power.

That thermal radiation from the sun can pass through glass is a matter of common experience. Prévost found that heat radiations from an ordinary flame could also pass through glass, ice, and various substances.

Melloni's apparatus for measuring the diathermancy of substances is shown in fig. 126. The screen B and the plate D being out of position, direct radiation was allowed to proceed from the lamp A through a hole in the screen C on to the thermopile E, and the deflection of the galvanometer was recorded.

The experiment was then repeated with a plate of the substance at D. The ratio between the second deflection and the first gave the fraction of the whole radiation that had passed through the plate, which is the measure of the diathermancy. Melloni enclosed his liquids in a trough with parallel sides, determining the effect of the

sides of the vessel by a preliminary experiment. He found that *pure water is very athermanous.*

Of all the substances tried, rock salt was the most diathermanous. It transmitted 92 per cent of the radiations that fell upon it. Sylvine (chloride of potassium) possesses the same characteristics. Hence the prisms and lenses used in investigations of thermal radiations are usually made of rock salt or of sylvine. A solution of

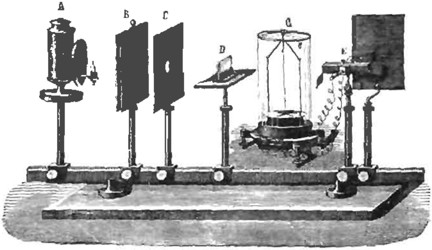

Fig. 126

iodine in bisulphide of carbon has been shown by Tyndall to be very diathermanous although it is opaque to light.

171. ABSORPTION.—Melloni measured the absorbing powers of different substances by means of a slight modification of the apparatus shown in fig. 121. Between the thermopile and the perforated screen he placed a thin copper disk, which was coated with lampblack on the side facing the pile, and on the other side with the substance whose absorbing power was to be measured.

It is clear that when a body which is exposed to radiation from a source of heat ceases to rise in temperature, the heat emitted must be equal to the heat absorbed. If, therefore, the plate absorbed per second a quantity of heat H, it radiated that quantity from its two faces. If the coefficient of emissivity be for lampblack E, and for the given substance E′, and τ be the excess of temperature of the plate above that of the air, then the heat radiated per second from unit area of the plate is $(E + E')\tau = H$, and of this heat $E\tau$ is radiated from the blackened face, and gives rise to a proportionate current in the thermopile. The coefficients E and E′ being known

the relative values of H for different substances are thus obtained from the indications of the thermo-pile. Proceeding in this way Melloni found that *the relative absorbing powers of different substances are exactly the same as their relative emissive powers.* As to this equality of absorbing and emissive power, it may be remarked that when a body receives or parts with heat by radiation, there is an interchange of energy between matter and ether, and the facility with which this interchange can take place appears to be independent of its direction.

Gases.—The absorptive power of gases and vapours has been investigated by Tyndall. Fig. 127 shows diagrammatically Tyndall's apparatus. A Leslie cube A contained water kept at 100° C. The heat radiated from the central part A′ of one side of the cube, passed

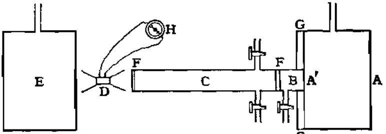

Fig. 127

along a tube BC (about 4 ft. in length), and fell on one face of a thermopile D, another cube E emitting radiation to the other face of the thermopile. A vacuum was maintained in the portion B of the tube, while the portion C contained the gas or vapour whose diathermancy was to be measured. The ends of C were closed by plates F of rock salt. Conduction of heat along the walls of B was prevented by a stream of cold water kept in circulation round the chamber G. With the tubes B and C both exhausted of air, the position of E was adjusted so that the galvanometer H attached to the thermopile showed no deflection, the radiation received from E being exactly equal to that received from A. Pure dry gas was then admitted into C and the deflection of the galvanometer observed. The relative opacities of the different gases were proportional to the deflections produced by their admission into C. Tyndall found that the admission of air, oxygen, nitrogen, and hydrogen produced no deflection, so that their diathermancy is very high and their absorptive powoı very small. The various compound gases that were tried, and also aqueous vapour, all gave deflections, some

of them very large, indicating that they absorbed much of the radiation.

Magnus made a series of experiments in which the thermopile was within the vessel that contained the gas under investigation. His results were very different from those of Tyndall, notably in respect to water vapour, the presence of which in air he found to be without effect on its diathermancy. Other investigators have obtained results differing considerably from those of both Tyndall and Magnus. Meteorological observations, however, appear to establish the fact of the high absorptive power of water vapour. And the whole of the observations go to prove that the radiating and absorbing powers are the same in each gas, although different in different gases. The presence of aqueous vapour in large quantities in the lower strata of the atmosphere thus tends to mitigate the intensity of the sun's rays, and to check radiation from the earth's surface. The low temperature prevailing, in the absence of direct sunshine, on the tops of high mountains is probably due, at least in part, to the diathermancy of the dry rarefied air, which allows radiation from the earth's surface to proceed unchecked. Vapours show great variation in absorbing power with temperature. As the temperature is raised their diathermancy becomes much greater.

According to Tyndall the absorbing power of compound gases is much greater than for elementary gases, whose molecular structure is more simple, from which it would appear that the energy is expended in increasing the motions of the atoms constituting the compound molecules rather than that of the molecules themselves.

172. **Selective Absorption.**—Early experiments showed that the absorbing power of a body is different for radiation from different sources. Thus, radiation from a Leslie's cube at 100° is quenched or absorbed to a large extent by many substances which allow radiations from a flame or from the sun to pass through in much greater proportion. The incident pencil usually contains radiations of very different wave lengths, which are present in different proportions according to the temperature of the source. Those radiations whose periods synchronize with the vibration periods of the molecules are absorbed, while those whose periods are very discordant pass on (Art. 237). Thus, glass absorbs waves of a long period, and consequently is athermanous to radiation from a source of low temperature, whereas it allows much of the radiation from the sun to pass through.

A substance absorbs almost completely those radiations which

the substance, when heated, would emit, on the same principle that *a number of stretched strings, tuned to a particular note, take up* the vibrations when that note is sounded and stop the passage of the sound-wave incident upon them. Thus rock salt is found to be opaque to radiations proceeding from hot rock salt.

A solution of permanganate of potash in water is transparent for the light waves coming from both ends of the light spectrum, but does not transmit the waves constituting the middle part of the spectrum.

Most substances behave in a somewhat similar way towards thermal radiation. Each substance transmits waves of certain lengths and is opaque to others. Lampblack is opaque to nearly all wave lengths, transmitting only the very long waves.

173. A study of the following table will illustrate several of the results obtained.

	Reflecting Power.	Relative Absorbing Powers. Source a cube at 100°.	Relative Emissive Powers at 100°.
Silver	97	13	3
Gold	95	13	3
Brass	96	13	7
Tin	85	13	—
Steel	83	13	17
Zinc	81	13	—
Platinum	80	13	17
Iron	77	13	—
Lampblack	—	100	100
White lead	—	100	100
Isinglass	—	91	—
Indian ink	—	85	85
Shellac	—	72	72

174. FORMATION OF DEW. — According to the generally received theory of dew, its formation is the result of the cooling *of the earth's surface by radiation during the night.* If radiation proceed sufficiently rapidly to chill the air near the ground below the dew-point, dew is deposited on the radiating surface. More dew is generally deposited on a clear than on a cloudy night, because the clouds radiate back to the earth nearly all the heat they receive from it, and thus prevent the chilling of the earth's surface. *The character of the surface also affects the result.* If the material be a good conductor of heat, the supply reaching it from the interior

of the earth may be sufficient to maintain its temperature in spite of the radiation, and in that case the air above the surface being maintained at a higher temperature is able to retain its moisture, and little or no dew is deposited. If, on the other hand, the surface be a good radiator and a bad conductor, it rapidly parts with its heat and receives little from the earth; it, therefore, becomes very cold, and much dew is deposited upon it. It is easily seen that the effect of wind must be to prevent the formation of dew by constantly substituting warmer air for the chilled air before the dew-point has been reached.

The above theory is probably incomplete. Recent evidence tends to show that dew may be deposited under quite different circumstances by the exhalation of vapour from the earth and from plants, and the condensation of this vapour upon the surfaces.

175. SOLAR RADIATION.—The rate at which the earth is receiving energy from the sun, and hence the rate at which the sun is radiating energy, may be estimated by *Pouillet's pyrheliometer* (fig. 128).

On the ends of long metal tube A are mounted a flat cylindrical vessel B of thin metal and a flat disk C of the same diameter. The calorimeter B is filled with water in which is the bulb of a thermometer whose stem passes along the tube A. The tube and its accessories are mounted on a suitable stand E by means of a universal joint D. The face B of the calorimeter is coated with lampblack, and the remainder of its surface is polished. The instrument is placed so that the axis of the tube A points to the centre of the sun, which is the case

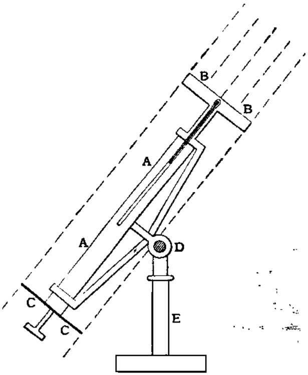

Fig. 128

when the shadow of B exactly covers C, and the rise of the thermometer in a convenient time is observed. The water-equivalent of the calorimeter being known, and correction made for radiation, the energy as measured by the number of calories H received per square centimetre per minute is calculated.

Observations are made with the sun at different heights above the horizon, from which the absorbing effect of the atmosphere is estimated, and the value for H outside our atmosphere is thus approximately found. This value is called the **solar constant.** The value found by Pouillet was 1·76.

Knowing the value of H, the rate at which the sun is emitting radiation is calculated. If a radiating sphere of radius r (in this case the radius of the sun) be surrounded by a hollow sphere of radius R (in this case the radius of the earth's orbit, assumed circular), then the energy that leaves a surface whose area is $4\pi r^2$ is received on a surface whose area is $4\pi R^2$. Hence

$$\frac{\text{the energy radiated per square centimetre by the sun}}{\text{the energy absorbed per square centimetre by the earth}} = \frac{4\pi R^2}{4\pi r^2} = \left(\frac{R}{r}\right)^2.$$

The radii of the sun and of the earth's orbit are very nearly 43×10^4 and 924×10^5 cm. respectively. Hence, taking Pouillet's value of the solar constant, the amount of thermal radiation leaving 1 sq. cm. of the surface of the sun in 1 min. is

$$1{\cdot}76 \times \left(\frac{924 \times 10^5}{43 \times 10^4}\right)^2 \text{ calories.}$$

The above figures give about 81,000 calories, which is equivalent to 7·5 horse-power.

Evaluations of the solar constant made by Violle with a different form of instrument, called by him an *actinometer*, gave the value 2·54 for the solar constant; and Langley, who had special facilities for estimating the effect of the earth's atmosphere, makes it about 3.

176. REFRACTION. THE SPECTRUM.—Let a parallel beam of radiant energy emitted from an electric arc K (fig. 129) or other convenient source pass through a narrow slit N and a prism M. Then it is found that if the light be focused by a lens L on a screen S'S placed in a suitable position on the farther side of the prism, there is seen upon the screen a multicoloured band of light VR, the colours being in order violet, indigo, blue, green, yellow, orange, red. The parallel beam NL has been **refracted** by the prism, i.e. caused to deviate from its original path, and also **dispersed,** i.e. spread out into

a band. On that part of the screen between V and S′, where under ordinary conditions the eye sees nothing, it is found that chemical action takes place on a photographic plate placed anywhere in that region. Between R and S, where also the eye sees nothing, a delicate thermometer or thermopile or radiometer shows a rise of temperature differing in amount in different parts of the region, just as the colours are different in different parts of the visible band. The whole band SS′ is the **radiation spectrum**; but as the three parts of it have to be investigated by us by different means, they are distinguished as the **chemical** or **actinic spectrum**, the **light spectrum**, and the **heat spectrum**. These spectra are not sharply divided from

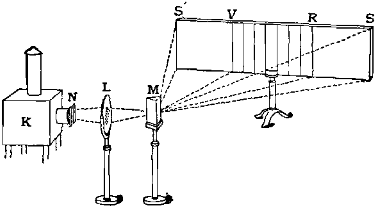

Fig. 120

each other, but overlap. The heating effect can be detected not only in the portion between R and S, known as the ultra-red or infra-red, but to a lesser degree through the light spectrum into the chemical region. Also photographic plates have been prepared which are affected not only by the violet and ultra-violet rays, but also by the radiation that constitutes the remainder of the visible spectrum and part of the thermal spectrum. But it may be generally stated that the most refrangible rays, i.e. those which are deviated most from their original direction by the prism, form the chemical spectrum, the least refrangible the heat spectrum, and the intermediate rays the light spectrum. Where the effects overlap they cannot be isolated. Jamin interposed layers of absorbing substances in different parts of the spectrum, and measuring the reduction thereby produced in the light and also in the heat, found that the light and heat were always reduced in the same ratio.

If a piece of uranium glass be placed in the ultra-violet region it

shines with a yellowish light: the substance has absorbed invisible rays and emits visible rays. This phenomenon is called **fluorescence.** In an experiment devised by Tyndall, the rays from an electric arc were passed through a rectangular glass vessel containing a solution of iodine in carbon bisulphide. The solution stopped all the light rays. The radiation that passed through the vessel was concentrated by a lens on to a piece of platinum foil. The foil became white-hot and emitted light. Thus the foil absorbed thermal radiation and gave out light radiation. This phenomenon is called **calorescence.** Such facts indicate that all radiation is essentially of the same character. The different effects that we perceive are due to difference in the lengths and periods of the waves that constitute the radiation, and to differences in the reactions to these various undulations of the molecules of matter on which they impinge.

The least refrangible rays have the greatest wave length. The greater the refrangibility the shorter the waves. The length of the waves is of the order of a thousandth of a millimetre or one forty-thousandth of an inch. The lengths of the waves constituting the light spectrum are known to a high degree of accuracy. They have usually been measured in tenth-metres (10^{-10} of a metre). The lengths of heat waves are usually expressed in microns, i.e. thousandths *of a millimetre, and the symbol adopted for a micron is* μ

$$1\ \mu = \cdot 001 \text{ mm. A tenth-metre is equal to } 10{,}000\ \mu.$$

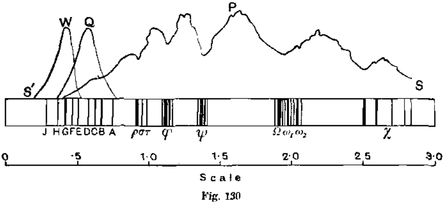

Fig. 130

Fig. 130 illustrates the general character of the results obtained by a preliminary examination of the spectrum. The length of the band S′S represents the distance on the screen along which the radiation passing through the prism is dispersed. The portion A to H represents the light spectrum, the chemical spectrum extends from

E to S′, and the thermal spectrum from H to beyond S. The heights of the curves WQP above the baseline at any particular point indicate the relative intensities of the effect at that point measured chemically for curve W, photometrically for Q, and thermally for P. The ordinates of the three curves, however, have no relation to each other, as the three kinds of effect are different, and are estimated by methods that are not comparable with each other. The approximate wave lengths (in microns) are shown at the base of the figure.

The details of the results vary in some respects according to the source of energy employed, because different sources emit the various rays in different proportions; and also according to the materials of which the lenses and prisms of the instruments are made, because different materials react differently on the different rays. For the investigation of the thermal spectrum the prisms and lenses are usually made of rock salt or sylvine, because these substances are found to pass about 90 per cent of the heat rays. If the source of light be the sun, dark lines A to H appear in the light spectrum, and bands where the heat is less intense are found also in the heat spectrum, as shown in the figure.

177. **The Infra-red Spectrum.**—This part of the spectrum has been investigated by various methods. Stefanik, employing a screen which absorbed the whole of the spectrum ordinarily visible, was able to detect by the eye radiations of much lower refrangibility than the ordinary red rays, as far as the rays of wave length 1 μ (fig. 130). Becquerel, allowing the radiation to fall on a plate coated with a phosphorescing substance, obtained phosphorescence effects as far as 1·4 μ, and detected the existence of dark bands.

Photography has also been employed. A spectroscope is used as in light observations, and in place of the eye a photographic plate is placed in the plane of the objective of the observing telescope. In the preparation of his plates Abney used an emulsion of silver bromide and collodion. Millochau, by employing a plate prepared with gelatine bromide and treated with malachite green, got photographs as far into the infra-red as ·95 μ on the scale.

Lehmann has photographed the spectrum as far as 2 μ. He used prisms of strongly refracting flint and a screen prepared with zinc sulphide. This screen having been exposed to blue light for thirty seconds, phosphoresced green. On exposure to the infra-red spectrum the phosphorescence was extinguished to a greater or less degree in different parts of the plate according to the energy of the radiation. The screen was then placed in contact with a photo-

graphic plate especially sensitive to green light and developed in the ordinary way. In these photographs bands appear, indicating the absence or diminished energy of rays of certain wave lengths, analogous to the dark lines in the visible solar spectrum.

Much of our knowledge of the infra-red spectrum is due to Langley, who invented the bolometer for these investigations. Fig. 131 may serve to give an idea of Langley's arrangements for investigating the infra-red spectrum of the sun. By means of a siderostat a beam of sunlight was directed on to the slit of a large horizontal collimating telescope T having an objective lens of rock-salt of 10 m. focal length. The beam was dispersed by a prism M

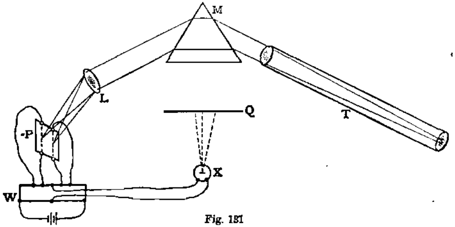

Fig. 131

of rock salt, and after its passage through M was focused by a lens L on to one of the wires of a bolometer P. The disturbance produced by the heating of one of the bolometer wires in the circuit of the Wheatstone's bridge W was indicated by a reflecting galvanometer X, whose mirror directed a spot of light on to a photographic plate Q. The prism M was mounted at the centre of a horizontal wheel which was rotated by clockwork, so that the spectrum slowly travelled across the bolometer wire, and this clockwork simultaneously gave the photographic plate a continuous vertical motion. Thus the heating effect experienced by the bolometer wire, as the spectrum travelled across it, was recorded by a thin wavy line on the photographic plate. The galvanometer employed had a quartz-fibre suspension and was extremely sensitive. The bolometer thread was $\frac{1}{20}$ mm. wide. The whole apparatus was so sensitive that Langley estimated that a difference of temperature as small as $\frac{1}{100000}$° C. was capable of detection. The machinery was so

geared that the spectrum travelled across the bolometer in two hours, and the trace on the photographic plate was 2 m. long. These traces are called by Langley **bolographs**.

The upper part of fig. 132 shows (one under the other) three of Langley's bolographs taken one after the other on the same plate on the same day. It is seen that the curves are all of the same character, differing only in their height above the base line. This height measures the energy of the radiation, which diminished with the diminishing altitude of the sun. Such curves can only be taken

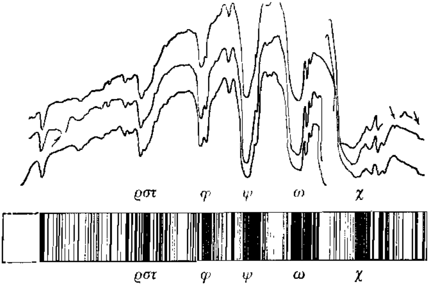

Fig. 132

during periods of sunshine, and even then there are often invisible clouds in the atmosphere which affect the curves, so that only by comparison of a number taken under the best conditions can the correct curve of thermal energy be obtained.

The line spectrum below the curves is obtained from the bolographs, a dark band in the spectrum corresponding to a depression in the curve, and a light band to a rise in the curve. The dark lines and bands are distinguished by letters. Their positions in the wave-length series is shown in fig. 130. Langley employed a special arrangement of spherical and cylindrical lenses which automatically recorded the linear equivalents of the rises and falls of the curve. Many of these linear spectra were then superposed one on the other by the process of composite photography, and thus the spectrum given was obtained. Most of the dark lines in the visible spectrum

are known to be due to absorption in the photosphere of the sun. Whether the dark bands and lines in the infra-red spectrum are due to absorption in the earth's atmosphere or to action near the sun is not certainly known. There are many inflections of the curve between 1 μ and 3 μ, and Langley recorded about 600 lines between 1·8 μ and 5·3 μ. He also found the spectrum to vary slightly with the season of the year.

178. MEASUREMENT OF WAVE LENGTH.—Let ABC (fig. 133) represent a prism, and ELMG the path of a ray passing through it in such a direction that LM is parallel to BC; then the angle KHG measures the deviation: call it D. Draw the normal NLO to the side AB. Then since the figure is symmetrical and ALO is a right angle, therefore the angle MLO $= \frac{1}{2}$ A.

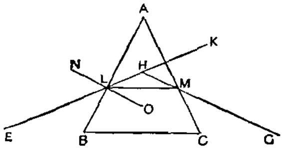

Fig. 133

Also, since D = 2HLO − 2MLO = 2HLO − A;

$$\therefore \text{ the angle HLO} = \tfrac{1}{2}(\text{A} + \text{D});$$

$$\therefore \frac{\text{HLO}}{\text{MLO}} \text{ or } \frac{\text{NLE}}{\text{MLO}} = \frac{\frac{1}{2}(\text{A} + \text{D})}{\frac{1}{2}\text{A}},$$

out the ratio $\frac{\sin \text{NLE}}{\sin \text{MLO}}$ is the definition of the index of refraction. Hence the index of refraction

$$n = \frac{\sin \frac{1}{2}(\text{A} + \text{D})}{\sin \frac{1}{2}\text{A}}.$$

Thus the index of refraction can be determined, whether of a ight ray or a dark ray, when the ray has been isolated.

The wave lengths of the light rays are known; and it is found hat for these rays the longer the wave the smaller is the refractive ndex, and the shorter the wave the greater the refractive index.

Various attempts have been made to establish a formula for light ays connecting the wave length with the refractive index. That f Briot,

$$\frac{1}{n^2} = \text{K}\lambda^2 + \text{A} + \frac{\text{B}}{\lambda^2} + \frac{\text{C}}{\lambda^4},$$

where n stands for the refractive index, λ the wave length of the ray, and K, A, B, and C constants, appears best to represent the facts. Assuming this expression to hold for thermal radiation, when the values of the constants have been determined, the wave length of any heat ray may be calculated from its index of refraction.

The wave lengths of heat rays are also directly measured, as are those of light rays, by a diffraction grating. Langley used a Rowland's concave grating — part of a spherical surface of polished metal. When a beam of radiation falls on such a grating, interference and diffraction take place, and a number of spectra are formed. In fig. 134, AC represents a section of the grating whose centre is O and radius of curvature OF. At D, the centre of the circle whose diameter is OF, three arms were hinged, of which DO carried the grating, DS the arrangements for transmitting a beam of radiation from S to O, and DB the bolometer B. Then the beam, proceeding from S and falling on the grating in the region near O, forms a series of spectra round the circumference of the circle OSB. These spectra may be numbered from 1 to q; then if λ be the wave length of any ray in the qth spectrum, i the angle of incidence of the light at O, d the angle of diffraction, and a the distance between two consecutive lines of the grating,

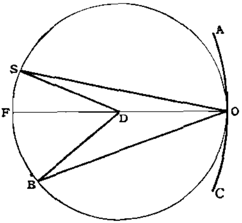

Fig. 134

$$q\lambda = a(\sin i - \sin d).$$

By this means Langley measured the wave length of rays up to $2{\cdot}5\ \mu$. The weakness of the diffraction method of measuring wave lengths is that with such a wide range of waves as that present in thermal radiations the various spectra soon overlap. They are moreover weak in energy. Hence the refraction method is often used.

The scale beneath the spectrum band in fig. 130 shows the approximate length of the waves measured in microns.

179. **Long Waves.**—Waves of much greater length than those referred to in the previous articles have been measured. Employing a cube of liquid as the source of radiation, and temperatures between

— 20° C. and 100° C., Langley estimated the length of the waves as between 15 μ and 5 μ.

Rubens and Nichols in one series of experiments employed as their radiating surface a layer of fluor-spar A (fig. 135) on platinum foil, which was maintained at any desired temperature. The radiation was successively reflected from three parallel surfaces B, C, and D of polished fluor-spar, and then received on the measuring instrument Q. The fluor-spar reflecting surfaces acted selectively on the radiation, so that the wave length of that which fell on Q was found to be 24·5 μ—nearly thirty times as long as the longest visible rays. With quartz surfaces they found that regular reflection took place of waves whose lengths were 7·4 μ, 8·5 μ, 9 μ, and 20·8 μ, but not of waves between those lengths. Mica showed similar results.

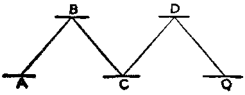

Fig 135

By successive reflection from polished surfaces of rock salt, Rubens has obtained still longer waves. The rays were found to be transmitted by quartz, so that using a quartz prism their index of refraction was measured. The value obtained was 2·19, and the wave length 56 μ.

The existence of absorption bands, demonstrated in these experiments, points to the existence of several systems of molecules vibrating in periods corresponding to the lengths of the absorbed waves (Art. 237).

180. SPECTRUM OF THE ELECTRIC ARC.—Using a bolometer of 75 ohms resistance, a galvanometer with quartz-fibre suspension, and a prism of silicate flint glass, Snow has investigated the spectrum of the electric arc between carbon points. It showed a large number of bands, each made up of numerous fine lines, five of the bands between ·7 μ and 1·5 μ being especially wide. Moll volatilized metallic salts in the arc, and projected its image, by means of a concave mirror, on to the slit of a spectroscope whose prism was of rock salt. The radiation was received on a linear thermopile of constantan and iron. The slit and thermopile were kept fixed and the prism slowly rotated, thus causing the spectrum to pass slowly over the thermopile. He thus obtained a curve of intensity ranging from ·7 μ to 6 μ. The refractive indices of different rays were measured, and their wave lengths calculated.

181. FULL RADIATION IN AN ENCLOSURE.—If a ther-

mometer be placed in an enclosure which is maintained at a constant temperature, it takes up the temperature of the enclosure. Masses of substances of different materials and different colours—e.g. iron, platinum, porcelain, glass—contained in a hollow in a hot fire, lose their distinctive appearances and outlines, and present to the eye one uniform white glare. Since the substances all look alike, they must each be emitting per unit area an equal quantity and quality of light radiation. They must also be receiving equal quantities, or differences would develop. And the same statement must be true of thermal radiations, or differences of temperature would result.

This conception of a uniform fully radiating enclosure has been of great service in the development of the theory of radiation. In its perfect form the enclosure may be regarded as a thick hollow sphere (fig. 136) with no aperture. For practical purposes it is of course necessary to have a small aperture through which the radiation from the interior may be examined by radiometers outside.

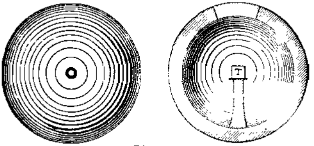

Fig. 136

Experiments made with such a shell show that whatever substance may be inside, the radiometer gives precisely the same indications for the same temperature. The only circumstance that affects the radiation is the temperature of the radiating substance.

Hence whether the radiation is luminous or non-luminous, the conclusion is that in such an enclosure a stream of radiation is proceeding in all directions, the quantity and quality of the stream depending on the temperature of the enclosure, and not at all on the materials composing it or enclosed within it. Each body emits exactly the same quantity and quality of radiation that it receives. Those that radiate much reflect little, and those that radiate little reflect much. A perfect equilibrium exists between the heat given out and the heat taken in by any element of the interior of the chamber, each element being supplied with those radiations which it reflects and which its own radiation lacks. Such an interior is said to act as a **full radiator**.

182. **Black Body.**—In everyday language a black body is one that does not reflect light that falls upon it. Experiment shows

that ordinarily a lampblack surface reflects little or none of the thermal radiations that fall upon it, but absorbs them all. Hence, abandoning the idea of optical effect, we may think of a **perfectly black body** as one which at any given moment is absorbing all the radiation of every wave length that is falling on it, reflecting none and transmitting none. Such a body is a full radiator, possessing the distinctive property of the interior of a fully radiating enclosure. The quantity of radiation proceeding from such a body is independent of the several circumstances that affect the results of Arts. 164 to 166, and represents very approximately the stream that is due to its own temperature only, and may therefore be used to measure that temperature.

The nearest practical approach to this theoretical perfectly black body is lampblack. This substance is therefore taken as the standard with which other radiating surfaces are compared. The quantity of heat that leaves such a surface is $1 \cdot 27 \times 10^{-12} \times \theta^4$ calories per square centimetre per second, θ being the absolute temperature.

Carbon in its more usual forms, and those metals, such as iron and copper, which on being heated become coated with a black oxide, approach the ideal condition. A perfectly black body cannot be prepared by artificial blackening. But any substances that are enclosed within hot furnaces, muffles, or combustion chambers, whose walls are at the same temperature as the contents, are at the time approximately black bodies in this sense.

183. **Radiation and Temperature.**—Many attempts have been made to find the connection between the temperature of a body and its rate of emitting radiant energy. The simple law of Newton and the more complicated expression obtained by Dulong and Petit (Art. 167) are only applicable under the circumstances and within the moderate temperature limits indicated in the experiments. Since the gas thermometer, the thermo-couple, and the electric-resistance thermometer have enabled much higher and lower temperatures to be measured with considerable accuracy, many investigations have been made with the object of determining the general relation between radiation and temperature.

In many experiments a strip of platinum has been used as the radiating surface. The strip may be heated by an electric current, and its temperature measured by a thermo-couple attached to it; or calculated by measuring its electrical resistance (the variation of resistance with temperature being independently known); or obtained from its expansion. The radiation proceeding from it may be mea-

sured by a bolometer or thermopile. Figures obtained by such and similar means have given different results, some making the total radiation proportional to θ^4, others to θ^5, and others to $\theta^{.7}$. These differences are probably due to departure from ideal conditions in the experiments, i.e. the radiating substances were not "black" bodies.

From his electro-magnetic theory of light Clerk-Maxwell deduced the result that there exists a pressure in the direction of propagation of light waves. This pressure has since been detected and measured by Lebedew and by Nichols and Hull. Starting from this fact, Bartoli and Boltzmann treated the radiation within a closed sphere as the working substance of a heat engine on the principles set forth in Chap. XXVI, and reached the result that in such an enclosure *the intensity of the total radiation proceeding from a body is proportional to the fourth power of its absolute temperature* (Art. **304**). This conclusion had previously been reached by Stefan from some observations of Tyndall, and from those of Dulong and Petit. This important law may be thus stated: Writing E for the total energy emitted per square centimetre per second, and E_λ for the energy per unit range of wave-length in the neighbourhood of λ,

$$E = \int_0^\infty E_\lambda d\lambda = a\theta^4 \text{ ....} (1)$$

θ being the absolute temperature and a a constant.

184. Wien and Planck have further developed the theory. When the temperature of a body is raised, the relative intensities of the energy of the various wave lengths change. Examining the spectrum of blackened copper at various temperatures between 40° C. and 800° C., Langley showed that as the temperature of a body rises, the spectrum is extended; radiations of greater and greater refrangibility gradually appear; and at the same time each element of the lower temperature radiation is increased in intensity. The energy of the radiation of higher refrangibility, i.e. of smaller wave length, increases in intensity more than that of lower refrangibility, so that if the maximum effect on the bolometer passed along the spectrum of a body at a certain temperature is at 1·0 μ, then on raising the temperature a certain amount the maximum effect is found at (say) ·9 μ. On Wien's theory the wave length which gives out maximum energy (where the bolometer gives the largest deflection) varies inversely as the absolute temperature, i.e.

$$\lambda_m = \frac{A}{\theta} \text{ ....} (2)$$

where λ_m stands for the wave length that is emitting maximum energy, and A is a constant. He further finds that the energy radiated through a small range of wave length $d\lambda$ near this maximum is proportional to the fifth power of the absolute temperature, i.e.

$$E_m d\lambda = A\ constant \times \theta^5 \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Planck has put forward a general expression dealing with the distribution of energy among the various wave lengths of the spectrum. If we take some definite wave length λ and consider the *total radiation* $E_\lambda d\lambda$ *emitted by a small range* $d\lambda$ *of wave lengths near* λ, then

$$E_\lambda d\lambda = C_1 \frac{\lambda^{-5}}{e^{\frac{C_2}{\lambda\theta}} - 1} d\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where C_1 and C_2 are constants and e is the base of the Napierian logarithms.

The constant C_2 is equal to 5A in the equation 2 above. Some investigators give its numerical value as 14700, others as 14200. C_1 is about 1000.

On these expressions is based the modern method of measuring the temperature of a body by means of the radiation that it emits.

185. Stefan's law as well as the further developments above mentioned have been experimentally tested by Wien, Lummer, and Pringsheim. They used a hollow sphere coated inside with lampblack for the lower temperatures, and with either oxide of iron or oxide of uranium for the higher temperatures. The temperature inside the sphere was measured by one of the methods indicated in Chap. XXVII, and the radiation by a bolometer placed near a small aperture in the sphere. They found that the total energy of radiation was proportional to the fourth power of the absolute temperature, thus verifying the Stefan-Boltzmann law (equation (1) above). Putting a prism of fluor-spar near the aperture and thus dispersing the radiation, they investigated the distribution of the energy at various temperatures and verified the law set forth in equation (3) above.

Kurlbaum arranged three porcelain tubes coaxially one outside the other, with air spaces between them. The central tube was wound over with thin platinum foil through which a strong electric current was passed. By varying the current, various temperatures up to about 1600° C. were obtained, the temperature at any time being measured by a carefully calibrated thermo-couple placed inside

the furnace. The radiation proceeding from the open end of such a tube very closely approximates to that of a fully radiating or black body to which the equations are applicable.

Valentiner employed a similar arrangement, measuring his temperatures, which ranged from 440° C. to 1550° C., both by a thermocouple and by a nitrogen thermometer.

The Stefan-Boltzmann law was closely verified by both these observers.

For bodies that are not "black" and are not in a fully radiating enclosure, the laws stated in equations (1) to (4) above do not hold good. Their radiation increases less rapidly with the temperature than does that of a black body, because reflection plays a part, so that its own radiation does not represent the whole stream coming from it.

186. EXAMPLES.

1. If the heat radiated per second from a black body varies as the fourth power of the absolute temperature, and amounts to 10 watts per square centimetre at 1000° C., find the temperature of the solar surface, assuming it to radiate 10,000 watts per square centimetre.

Let the temperature be $x°$, then by Stefan's law $E = a\theta^4$;

$$\therefore 10 = a(1273)^4, \quad \text{...(1)}$$
$$\text{and } 10000 = a(x)^4; \quad \text{...(2)}$$
$$\therefore 1000 = \frac{x^4}{(1273)^4};$$
$$\therefore x = 1273(1000)^{\cdot 4}$$
$$= 7154° \text{ absolute}$$
$$= 7430° \text{ C.}$$

2. Compare the amounts of heat lost per second by bodies at 627° C. and 127° C. respectively in an evacuated vessel which is kept at 27° C.

The absolute temperatures are 900°, 400°, and 300°.

$$\text{For the first body } E_1 = a(900^4 - 300^4)$$
$$= a \times 100^4 \times 6480.$$
$$\text{For the second body } E_2 = a(400^4 - 300^4)$$
$$= a \times 100^4 \times 175;$$
$$\therefore \frac{E_1}{E_2} = \frac{6480}{175} = 37.$$

3. Find approximately the thermal emissivity of a block of iron 1 cm. cube, specific heat ·12, and density 8, if it takes 5 min. to cool from 60° C. to 50° C. in an enclosure at 0° C.

Total heat emitted $= 8 \times \cdot 12 \times 10 = 9\cdot 6$ units.
Heat emitted per second $= 9\cdot 6 \div 300 = \cdot 032$ unit.
" " " per unit area $= \cdot 0053$ "
The average number of degrees difference
between the hot body and the enclosure $= 55$ degrees.
$\therefore$ Emissivity (Art. 166) $= \cdot 0053 \div 55 = \cdot 0001$ nearly.

4. *A wire ·1 cm. in diameter carrying a current of 10 amperes is found to reach* a steady temperature of 100° C. Assuming the specific resistance of the material as $2{\cdot}1 \times 10^{-4}$ ohms per centimetre cube, and the value of J as $4{\cdot}2 \times 10^{6}$ ergs, determine the amount of heat emitted at 100° C. by a square centimetre of the surface.

Taking 1 cm. length of the wire, the

Sectional area	$= \pi\left(\frac{\cdot 1}{2}\right)^2 = \cdot 0025\pi$ sq. cm.
Length	$= 1$ cm.
Surface area	$= \pi \div 10$.
Specific resistance	$= 2{\cdot}1 \times 10^{-4}$.
∴ its electrical resistance (r)	$= 2{\cdot}1 \times 10^{-4} \div \cdot 0025\pi$,
and the time (t)	$= 1$ sec.
∴ Heat produced	$= C^2 rt \times \cdot 24$
	$= 210 \times \cdot 24 \div 25\pi$.
∴ $\dfrac{\text{Heat}}{\text{Surface area}}$	$= \dfrac{20{\cdot}16}{\pi^2} = 2{\cdot}03$.

QUESTIONS AND EXERCISES

1. Explain how to determine the emissive powers and the absorbing powers of substances for radiant heat. State the relations which exist between them, and show how these are experimentally verified.
2. Describe and explain the action of Crookes' radiometer.
3. Describe experiments by which the laws of cooling may be found, and give an account of the results obtained.
   State the influence on the rate of cooling of a body in air, of (1) its temperature; (2) its mass; (3) its specific heat.
4. How is the deposition of dew affected by the presence or absence of clouds in the sky?
   A table knife with a black handle is left exposed to the atmosphere in the evening; which part of the knife, the handle or the blade, will be first covered with dew? Give reasons for your answer.
5. Trace the analogies, as far as they have been experimentally determined, between luminous and non-luminous radiation.
6. How would you investigate the laws of reflection and refraction of dark radiation?
7. How can the length of a dark ray be determined?
8. Explain the fact that the quality of the radiation inside an enclosure at a uniform temperature is independent of the nature of the surface.
9. Write a short account of the variation of the radiation from a hot body with the temperature. How may a standard radiator be produced?
10. The term "radiant heat" is sometimes applied to the radiation from a hot body. Is the term appropriate? Give reasons for your opinion.
11. Describe experiments by which the positions of the absorption bands in the extreme infra-red due to such substances as quartz and fluor-spar have been determined.

CHAPTER XVII

MEASUREMENT OF TEMPERATURE

187. METHODS OF ESTIMATING TEMPERATURES.—In Chap. II was given a description of the mercurial thermometer, the instrument by which, owing to its great practical convenience, ordinary temperatures are usually measured, its use being based on the assumption that change of volume may be taken to register change of temperature. It has been pointed out in subsequent chapters that other properties of bodies change with the temperature according to laws more or less accurately known. Any one of these may furnish the basis of temperature measurement. Hence we find in use the following modes of measuring temperature:

(i) **By change of volume**, the substance being solid, liquid, or gaseous. Of liquids the most commonly employed are mercury, alcohol, pentane, toluene, or petroleum ether enclosed in glass, and of gases, air, nitrogen, or hydrogen, contained within a glass or porcelain reservoir. The rough indications afforded by solids are usually based on change of length.

(ii) **By change of pressure** of gases.

(iii) **By heat evolved.** When a portion of some substance is taken from a place of high temperature and immersed in water. This is a calorimeter method.

(iv) **By change of electrical properties**; either of the thermo-electric force, or of resistance, as in the case of Langley's bolometer and the platinum thermometer.

(v) By the **radiation** emitted by a hot body.

188. LIQUIDS AND SOLIDS AS THERMOMETRIC SUBSTANCES.—As to these the following observations must be made. Whatever substance is employed, the method of graduation, which marks the freezing point $x°$ and the boiling point $y°$, and then divides the space between into $y - x$ equal parts, takes as its basis the mean coefficient of dilatation of the substance between those limits. And in the case of liquids this coefficient is the apparent coefficient. It has already been pointed out that the use of such a mean coefficient does not enable the relative volumes of the substance at any two intermediate points to be accurately ascertained. And of course in such a thermometer an error as to the volume of the substance leads to an error in the estimation of temperature.

Moreover, each substance (solid or liquid) follows a law of expan-

sion peculiar to itself in regard to the extent of its deviation from simple proportionality to the temperature. Therefore two thermometers of different substances cannot agree in their indications anywhere except at the fixed points.

189. Choice of a Thermometric Substance.—The theory of heat does not enable any rational explanation to be given of thermometers which purport to measure temperature by the change of volume of a solid or liquid.

A more rational supposition is that the rise of temperature of a body is proportional to the heat absorbed by it. Dulong and Petit therefore compared the changes of volume undergone by different bodies when heated with the quantities of heat absorbed in the process. They arrived at the conclusion that the change of volume was not proportional to the heat absorbed in the case of solids and liquids, but that this proportionality held good in the case of the permanent gases.

In Regnault's determination of the absolute expansion of mercury the temperatures were measured by the air thermometer, and the results allowed of a comparison between air and mercury.

TEMPERATURE AS INDICATED BY—

Volume of Air.	Volume of Mercury.	An Air Thermometer.	A Mercury Thermometer.
0° C.	0·000° C.	—	—
40°	39·67°	—	—
80°	79·78°	—	—
100°	100·00°	100·00	100·00
160°	161·33°	160·00	159·74
220°	223·67°	220·00	219·80
280°	287·00°	280·00	280·52

The first two columns are a comparison of absolute volumes, the last two of actual readings. The latter is useless except for the particular mercury thermometer employed, since the indications of the latter instrument vary with the kind of glass of which it is made.

Theoretical reasons thus point to air or one of the more permanent gases as the best thermometric substance.

The conditions that should be fulfilled by a good thermometric substance are as follows:—

(i) In order that the thermometer may enable us to compare quantities of heat, the changes of volume produced by equal incre-

ments of heat, should be the same at all temperatures, i.e. *the coefficient of expansion and the specific heat should be constant*, i.e. independent of the temperature, as measured on the absolute scale.

(ii) In order that the instrument may be sensitive, the substance should expand considerably and rapidly on a small addition of heat, i.e. *it should have a large coefficient of expansion, small thermal capacity, and high conductivity.*

(iii) In order that the thermometer may be of general use, *the substance should retain the same physical state through a wide range of temperature.*

190. TEMPERATURE MEASURED BY THE INDICATIONS OF SOLIDS.—There is no ordinary solid substance that even approximately fulfils the above conditions.

The change of length taking place in a solid bar when heated has, however, been employed as a means of estimating high temperatures. Wedgwood employed a pellet of dried clay, and estimated his temperatures by observing the amount of contraction that took place on heating. Brongniart employed an iron bar embedded in a porcelain slab. One end of the bar was fixed in the porcelain, the other end was free, and in its motion turned an index placed outside the furnace.

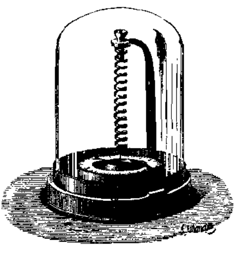

Fig. 137

Breguet's thermometer is shown in fig. 137.

A thin strip of silver is soldered to one side of a strip of gold, and a strip of platinum to the other side. This compound strip is then coiled into a spiral, of which the upper end is fastened to a support and the lower end carries a needle. When the temperature of the spiral changes it coils or uncoils and thus turns the index, beneath which is placed a graduated circle on which the temperatures are marked.

All such thermometers are open to the great objection that changes take place in the condition of metals, so that after heating, they do not return exactly to their original condition when allowed to cool to the original temperature.

191. LIQUID THERMOMETERS.—Of liquids, water is an unsuitable substance, because with a temperature range of only 100° it has a high thermal capacity and a temperature of maximum density. Moreover it adheres to glass.

For low temperatures use has often been made of thermometers containing alcohol, chloride of phosphorus, or sulphide of carbon, the graduation of the instruments being usually made by comparison with the air thermometer. The values $-130°$, $-111°$, and $-110°$ have been given as the temperatures at which, according to the indications of the hydrogen thermometer, these liquids respectively solidify under atmospheric pressure.

Alcohol is slower in its action than mercury because it is a worse conductor. The degrees on its scale are made longer at the higher than at the lower temperatures, because there is a considerable increase in its rate of expansion with rise of temperature (Art. 64). Toluene, petroleum ether, and pentane are also suitable liquids that can be relied on down to temperatures approaching $-190°$ C.

192. The Mercury Thermometer.—Liquid mercury has a fairly wide range of temperature, a low thermal capacity, is a good conductor of heat, does not adhere to glass, and may easily be obtained pure. Its coefficient of expansion and specific heat are not quite constant. As to the coefficient of expansion, however, it may be noted that both glass and mercury expand more quickly at high than at low temperatures. The absolute amount of expansion of mercury between 99° and 100°, for example, is about 3 per cent greater than the expansion between 0° and 1°, but the capacity of the glass envelope is also larger at the higher temperature; so that between 0° and 100° the rate of apparent expansion of the mercury is nearly uniform.

One of the most important desiderata in thermometry, viz. the comparability of temperatures as registered by different instruments, may be fulfilled with mercury thermometers if certain precautions be observed.

We have already seen (Art. 7) that allowance must be made for inequalities in the bore of the stem, for deviation from the standard height of the barometer when the boiling-point is marked, and for the temperature of the stem when that is not the same as that of the bulb. The heat capacity of the thermometer needs to be allowed for in experiments where that is likely to lower the temperature that is to be measured. There is also a certain lag in the movement of the mercury in the case of a rapidly changing temperature, and the mer-

cury moves in jerks owing to the surface tension between the liquid and the glass. Avoidance of parallax in taking any reading is also essential to accuracy.

Glass.—A very important matter in the construction is the choice and treatment of the glass. Great discrepancies may otherwise occur, especially at high temperatures. With all mercury thermometers there takes place, after heating, a gradual contraction of the bulb, which leads to an error in the position of the zero. In every important measurement it is necessary to take the zero reading before the reading in question. Observations made on Joule's thermometers at intervals during forty years showed that the process of contraction continued at a gradually decreasing rate throughout that period, the amount of change in thirty-eight years amounting to 1° F.

Fused silica is now much used. The glass known as *verre dur* is one of the best. Schott's normal thermometer glass, known as 16^{III}, can be used with good results up to 450° C. Another borosilicate glass, 59^{III}, is extensively employed for thermometers reading up to 500° or 550° C. As, however, the "after-working" effect is always present to some extent, attempts have been made to compensate for it. To this end the bulb of the thermometer is sometimes made in the form shown in fig. 138, with a rod projecting into the reservoir. This rod is made of glass whose after-working is greater than that of which the thermometer is composed, and its volume bears such a ratio to that of the surrounding envelope that the two changes of volume as nearly as possible compensate each other. Glasses that contain either potassium or sodium are most free from this after-working effect.

Fig. 138

If the bulbs are blown on the tubes certain constituents of the glass in the bulb are thereby vaporized, and there is thus produced a difference between the bulb and the stem. The bulbs are therefore sometimes made separately of thinner glass, and are afterwards welded on to the stem.

Annealing.—In every thermometer that is intended to indicate temperatures over 100° C. the glass should be annealed by being kept for several days at a temperature of about 450° C. and then gradually cooled during three or four days.

Pressure.—Mercury thermometers intended to measure high temperatures have, in the space above the mercury, nitrogen or carbon-

dioxide gas at high pressure. For temperatures up to 300° C. a pressure of 1 atmosphere is sufficient, for 450° about $4\frac{1}{2}$ atmospheres, *and for 550° about 20 atmospheres. This great internal pressure* of course increases the size of the bulb, and such thermometers need special graduation. But the boiling-point of sulphur is known very accurately as 444·6° C., and such points enable the thermometer to be correctly graduated.

The readings of sensitive thermometers are also affected by the pressure of the mercury, which tends to enlarge the reservoir. The extent of the error due to this cause may be found by comparing *readings of the thermometer at various temperatures, first in a hori*zontal and then in a vertical position. Pressure on the outside also affects such thermometers. To find the error due to this cause the thermometer is placed in a suitable liquid, e.g. glycerine, contained in a closed vessel, within which by means of a pump various pressures can be obtained, and readings taken at various pressures with the temperature constant.

193. GASEOUS THERMOMETERS.—The only substances that through *a wide range of temperature retain the same state*, and change in volume or pressure in the same way, are the permanent gases. Hence their special value as thermometric substances. Thermometers containing air, hydrogen or nitrogen, whether under the same or different pressures, all indicate exactly the same temperature whatever (above a certain limit) that temperature may be. The simplest form of the air thermometer one can imagine is a long tube of uniform bore containing a movable *pellet of mercury, the lower surface of which would be marked* 273° when the instrument was in melting ice, and 373° when in steam from water boiling under 760 mm. pressure. The graduation marks beyond these limits would be of the same length as within them.

Such an instrument would, however, be open to several practical objections. After many trials Regnault decided that it was better to keep the air at constant volume and deduce the temperature from *the variation of pressure.*

The form of *constant-volume* thermometer introduced by Jolly is shown in fig. 139. A globe A is connected by a bent capillary tube AB with a piece of indiarubber tubing BCD, which is prolonged by a straight glass tube DE open at E to the atmosphere. At B and D the tubes are clamped by the side of scales on to a board placed vertically. The globe A is filled with dry air and the tube BCD

with mercury, which also extends a short distance up the vertical glass tube. The indications of the instrument are interpreted in the following manner. The globe being in melting ice the clamp D is raised or lowered until the mercury above B stands at a fixed mark. Then the pressure of the air in the globe is measured by the sum of the height of the barometric column, and the height of the mercury surface F above the fixed mark.

If A be then raised to some higher temperature, the clamp D is raised until the mercury again stands at the fixed mark above B and the pressure of the air in A is again obtained.

The relation between these pressures gives the relation between the temperatures, of which the first is known.

In this instrument the tube AB should be of small bore, otherwise at rather high temperatures a somewhat uncertain correction becomes necessary owing to the fact that this tube is not at the temperature of the globe. The air thermometer possesses the advantage that the changes of volume are so great that the changes of the vessel are negligibly small, the expansion of air being 160 times that of glass.

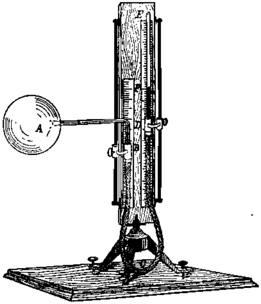

Fig. 139

The typical form of the *constant-pressure gas thermometer* is that shown in fig. 31. A modified form, which is more convenient and accurate in use, is shown in fig. 140. A is the thermometer bulb connected by a tube of small bore B to one limb of a U-tube C, to the other limb of which, by means of a tube B′, is attached a bulb A′ of exactly the same dimensions as A. Between A and C is inserted a bulb D which is filled with mercury that can be drawn off by a tap. The U-tube C is filled to a convenient height with oil. The tubes B and B′ are exactly similar, and lie parallel and close together.

The bulbs A, A′ and the pipes B, B′ being filled with dry gas, the whole apparatus is placed in melting ice and the mercury in D

adjusted until the oil stands at the same height in the two arms of C. The instrument is then ready for use. The bulb A is placed in the space of which the temperature is to be measured (supposed higher than 0° C.), and the remainder of the apparatus is kept at 0° C. At the higher temperature the gas expelled from A is compensated for by drawing off mercury from D until the liquid again stands at the same height in the two arms C, C, the volume of mercury drawn off measuring the volume of gas expelled from A. Then since the masses of air on the two sides of the pressure gauge are the same, and these masses are at the same pressure P, and the

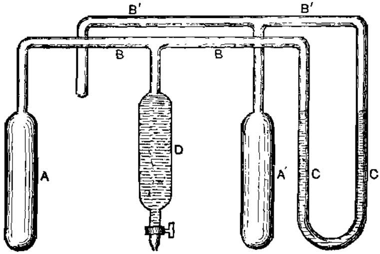

Fig 140

volumes of the corresponding parts of the apparatus are also equal, if V and V_1 represent the volume of the bulb A at freezing-point and at absolute temperature θ respectively, and v the volume of the expelled mercury, we have

$$P\left(\frac{V_1}{\theta} + \frac{v}{273}\right) = P\frac{V}{273}$$

$$\therefore \frac{\theta}{273} = \frac{V_1}{V - v}.$$

The constant-pressure thermometer has the disadvantage that its sensitiveness changes somewhat with the change of volume of the gas, and the constant-volume thermometer that the volume of the bulb increases with change of pressure.

Investigations have recently been made by Holborn and Day as to the best material for the reservoirs of gas thermometers. For

temperatures up to about 500° C. bulbs made of 59^{III} Jena borosilicate glass and containing hydrogen proved very satisfactory, the zero keeping constant after repeated heatings and coolings. Porcelain bulbs containing either hydrogen or nitrogen were unsatisfactory at such temperatures as 1100° C., the zero rising and the expansion being of a changeable character. The glazed surface of the porcelain melted at about 1100° C., and at about 1450° C. the porcelain itself softened. *With bulbs of platinum it is found that at high temperatures* hydrogen passes through the platinum but nitrogen does not.

For temperatures such as those mentioned, they found that a platinum-iridium vessel containing nitrogen was most free from such defects; but even with this arrangement, in some cases combustion products passed through the bulb wall. Hence investigations at such temperatures as 1100° C. to 1400° C. are best conducted, whenever possible, in an electrically heated furnace, which may be filled with a gas that is chemically inert.

The air thermometer is inconvenient for general use, as for each temperature a delicate experiment is necessary. In practice a method often adopted is to compare the liquid thermometer with the air thermometer within the limits of the readings which are actually taken by the liquid thermometer.

The absolute scale as realized by the constant-volume hydrogen thermometer appears to be the best ultimate standard to which all others are referred.

194. Deville and Troost in their investigations on vapour densities determined their high temperatures as follows.

They placed some iodine within a porcelain reservoir which had a fine neck that projected from the furnace. As the iodine passed into vapour it was driven out, carrying the air with it. When all the iodine was vaporized the neck was sealed and the instrument removed and cooled. The quantity of the iodine inside was then determined by weighing; the volume of the reservoir was known; the relative density of iodine vapour is 8·7. At the high temperatures employed, iodine vapour obeys the gaseous laws very nearly as accurately as air. From these data, therefore, the mass of air occupying a known volume at a known pressure (given by the barometer) is approximately obtained, whence the temperature is deduced.

Regnault employed the same method, his reservoir being of iron and his vapour that of mercury. The reason for employing heavy vapours in such experiments is that the errors of weighing bear a

smaller ratio to the mass to be weighed, and the result is therefore more accurate. The method is evidently applicable only to the determination of some one particular temperature.

195. ELECTRICAL METHODS.—At temperatures below about -150° C. the permanent gases deviate so much from Boyle's law that their use as thermometric substances involves special investigations. Electrical methods have been resorted to for the estimation of such temperatures, as well as of very high temperatures.

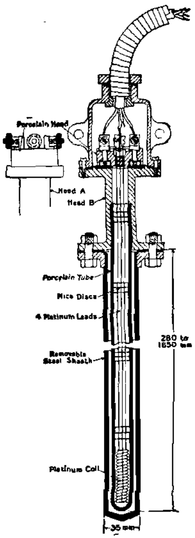

Fig. 141

Variation of Electrical Resistance.—The electrical resistance of metals increases with rise of temperature (Art. 134). Owing to the extreme precision attainable in electrical methods of measurement it has been proposed to utilize this property of metals to indicate temperature, and with this object in view the behaviour of platinum has been especially studied. Sir Wm. Siemens' pyrometer consists of a platinum wire, whose resistance r_0 at 0° C. is accurately known, wound on a small porcelain cylinder enclosed in a tube of iron or platinum. The wire, which forms part of an electric circuit, is placed in the furnace and its resistance r_t again measured.

The temperature is then deduced from the formula representing the variation of resistance with temperature as previously determined. Siemens' pyrometer is not, however, an accurate instrument owing to its mode of construction.

The perfecting of the electric-resistance thermometer is due to *Callendar*. *He found that a wire of pure soft annealed platinum may have its temperature varied very considerably and yet always have the same resistance when brought back to any particular temperature, and that all such wires behave very nearly alike.*

Fig. 141 shows one of these thermometers. In some of the more recent forms a thin platinum wire is wound on a rod of quartz, which is then introduced into a thin tube of quartz, to which it is fused, so that the wire is embedded in quartz, a material which is capable of withstanding abrupt changes of temperature. The wire is surrounded by protecting tubes of various materials, such as asbestos, porcelain, or steel, according to the degree of necessity for protection from destructive gases or mechanical injury which may occur in its use. Thick leads connect the wire with the terminals at the other end of the instrument, and two similar compensating

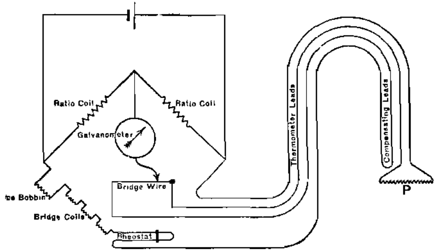

Fig. 142

leads connected to each other at the end also run throughout the length of the tube to two other terminals. Such instruments are used to measure temperatures from -150° C. to about 1200° C. or 1400° C., and within their range give accurate results.

The *method of connecting the instrument to its electric circuit* is shown in fig. 142. The ratio coils are of equal resistance. The resistance of the thermometer coil P is generally adjusted so that between 0° C. and 100° C. the change in its resistance is exactly 1 ohm. Of the two variable arms of the Wheatstone's bridge one contains the thermometer wire P, its leads, and a portion of the bridge wire; the other contains balancing resistances, compensating leads, and the remainder of the bridge wire. The "*ice bobbin*" shown is a coil that possesses exactly the same resistance as does the thermometer wire P at 0° C., so that any resistance added to this arm indicates the change of resistance of the thermometer wire

due to change of temperature; and as every additional resistance of 1 ohm indicates 100° rise in temperature, the temperature reading is obtained by simply regarding each ·01 ohm as a degree. These temperatures thus read are, however, on the platinum scale. This scale is obtained as follows. A horizontal line is drawn, and marked in degrees (fig. 143). The resistance of the wire is accurately determined at 0 C. and 100° C., and ordinates A and B are drawn representing these values. The line PQ is then drawn, and continued in both directions. When the value of the resistance is that indicated by C, the temperature on the platinum scale is 200°. To compare temperatures on the platinum scale with those on the gas scale a reduction is therefore necessary, which is given by the formula

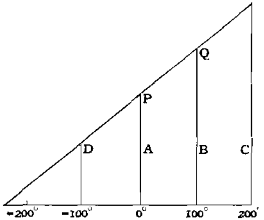

Fig. 143

$$\Delta = \delta\left(\frac{T}{100} - 1\right)\frac{T}{100},$$

δ having the value 1·5 for pure platinum, T being the temperature on the platinum scale, and Δ the correction required.

The following figures illustrate the divergence between the scales:—

Platinum Scale.	Gas Scale.	Platinum Scale.	Gas Scale.
0°	0° C.	200°	203·1° C.
50°	49·6°	500°	534·9°
100°	100°	1000°	1197°

Harker and Chappuis on comparing one of these thermometers with the mercury standards of the International Bureau from − 23° to 80°, and with a nitrogen thermometer up to 1000° C. found a close agreement between the standards and the corrected values of the resistance thermometer.

Dewar compared the behaviour of eight resistance thermometers made of different pure metals with the hydrogen thermometer at low temperatures. He found that their resistances diminished

towards an asymptotic value below which no further cooling reduced them, the law which holds for higher temperatures not holding good for very low temperatures. Onnes also found that a special formula was necessary for platinum and gold thermometers below $-100°$ C. Hence the resistance thermometer is only of limited usefulness for measurement of very low temperatures.

The resistance thermometer is especially valuable for the measurement of temperatures (within its limits) in inaccessible places, since the leads may be brought any distance to the instruments. Thus they have been used to obtain records of the variation of underground temperatures, as they may be left buried for years and their changes indicated by a recorder tracing a line on a revolving drum.

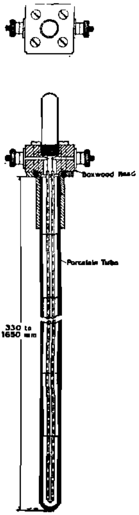

Fig. 144

Thermo-electric Couples.—When the law connecting the thermo-electric force of any couple with the temperatures of the junctions is accurately known, such a couple may in turn be used to measure temperatures. (Art. 135.)

If one junction is at 0° C. and the other at $\tau°$ C., then the electro-motive force is represented by the formula

$$\log E = A \log \tau + B$$

where E is the electromotive force of the couple in millivolts, and A and B are constants. For a couple of platinum and platinum-rhodium the approximate values are of A = 1·19 and of B = ·52, and for other couples the constants are of the same order of magnitude.

To measure moderate temperatures in inaccessible places, such as the bottom of the sea, it is only necessary to place one junction at the place in question and the other in a bath whose temperature can be regulated. When the galvanometer in the circuit shows no current, then the temperature of the two junctions is the same; the temperature of the bath being of course known, that of the other junction is known.

The great difficulty is to find metals that are sufficiently homogeneous in their structure. A piece of wire that has been knotted

or twisted or stretched or hammered behaves to a piece that has not been thus treated as though it were a different metal, and the uncertainty attaching to this may amount to 10 per cent of the quantity to be measured.

The form of a thermo-electric thermometer is shown in fig. 144. The two wires are enclosed in a porcelain tube, and if necessary this is surrounded by an outer tube of steel. The wires are connected to two terminals at the head of the instrument, by means of which it is connected to its electric circuit. This may be a considerable

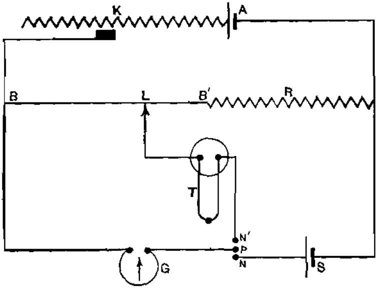

Fig. 145

distance away, and it is of course necessary that the cold junction should be kept cold. Fig. 145 shows the arrangement of the circuit. An accumulator A maintains a steady current round the circuit AKBB'R, K being an adjustable rheostat, BB' a wire of known resistance per unit length, and R a suitable resistance. The function of this circuit is to maintain a steady difference of potential between the points BB'. The amount of this potential difference is determined by means of the circuit SNPGBR, round which a current may be passed from the standard cell S, whose electromotive force is very accurately known. When P and N are joined and these two circuits are in operation, the rheostat K is adjusted until the galvanometer G shows no deflection. When this is the case, the difference of potential between B and the extreme terminal of R is that of the standard cell, and the fall along the measured distance BB' becomes

known. If now the contact P be moved to N′, and the contact L adjusted so that the galvanometer shows no deflection, we know the electromotive force produced by the thermo-couple T from the length of the wire BL included in its circuit, and the temperature is calculated from the equation given above.

For temperatures up to 500° C. a copper-constantan couple is best, as it gives a larger potential difference per degree; one of platinum and platinum-iridium may be relied on up to 1000° C., and one of platinum and platinum-rhodium to about 1400° C. Berthelot compared the results from two different couples for five melting-points and eight boiling-points up to 1100° C. and found that they did not differ by more than 2° C. He determined the constants A and B above by taking observations of E at the melting-points of zinc and gold, which may be regarded as determined at 419° C. and 1064° C. respectively.

196. **Radiation Pyrometers.**—In this class of instruments the temperature of a source of radiation such as a furnace is deduced from observations on the radiations that it emits. There are two chief forms of radiation pyrometer. In one form the whole radiation of all wave lengths that is received by the instrument is concentrated on some form of thermometer, and the basis of the temperature determination is the Stefan-Boltzmann law (Art. 183)

$$E = a(\theta_1^4 - \theta_2^4)$$

where E is the energy radiated by a black body at absolute temperature θ_1 to another body at absolute temperature θ_2, and a is a constant depending on the units employed.

The other form is photometric, and uses only radiation of one wave length or of a small group of adjacent waves.

The photometric instruments compare the intensity of the red light rays emitted from the source with the intensity of the red rays given by a standard lamp. By using only these rays the complications that ensue owing to the changes that take place in the light radiations, and therefore in the colour of the light, as the temperature of a body rises are avoided. Red light has also the advantage that it is the first to appear as the temperature of a body rises, and hence the instrument begins to be useful at the comparatively low temperatures at which luminosity begins. The wave length of the red light which corresponds to the hydrogen line ($\lambda = \cdot 656\mu$) is a convenient standard.

As the temperature of a hot body rises the intensity of the

particular radiation selected increases, according to Planck's law (Art. 184). Thus the relation between two temperatures becomes known from the relation between the intensities of the red light emitted. In making the comparison, if E_1 and E_2 are the intensities of the light emitted at absolute temperatures θ_1 and θ_2,

$$\text{then } \log_e \frac{E_2}{E_1} = \frac{C}{\lambda}\left\{\frac{1}{\theta_1} - \frac{1}{\theta_2}\right\}$$

where C is a constant. The constant C is determined by taking observations at temperatures which are measured by a gas thermometer or standardized thermo-couple; and having been determined, is in turn used to find θ_1 when θ_2 is known.

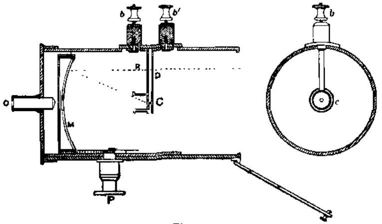

Fig. 146

Radiation pyrometers are of especial service for temperatures above 1200° C. Between that temperature and 2000°, measurements may be relied on within a maximum error of a few per cent, depending on the conditions of the experiment. Where the numerical value of the temperature is not required, but merely the test whether two temperatures are the same, the result is quite satisfactory.

In the **Féry radiation pyrometer**, temperatures are estimated by the comparison of the total thermal energy emitted by bodies at different temperatures. A section of the instrument is shown in fig. 146. It consists of a short reflecting telescope, which is directed towards the body whose temperature is to be measured. The radiation after passing along the tube falls upon a concave mirror M, and is concentrated by the mirror upon a thermo-couple C placed at its focus. The indications of the galvanometer attached to the thermo-

couple give the temperature of the source of radiation. The thermo-couple is made of copper-constantan arranged in the form of a cross, from which two brass strips DR lead to the terminals b, b'. The position of the mirror is capable of adjustment by the rack and pinion P. On looking through the eye-piece O (the concave mirror is, of course, pierced at the centre), the thermo-couple is seen in the form of a black disk in the centre of the field of view. The instrument is turned on to an observation hole in a furnace wall fig. 147, and the mirror is adjusted till an image of the hole slightly larger than the black disk is formed on the disk. Under these conditions the rise of temperature of the thermo-couple is proportional to the amount of radiant energy that enters the telescope tube. When measuring very high temperatures, such as 2000° C., a diaphragm is placed so as partially to cover the aperture of the telescope, thus reducing the readings in a simple known ratio.

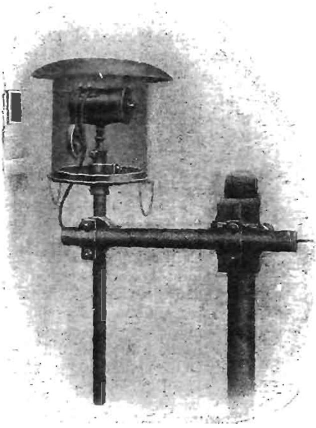

Fig. 147

If the radiation pyrometer be turned successively on two black bodies whose absolute temperatures are θ_1 and θ_2, and if the deflections of the galvanometer are d_1 and d_2, then

$$\frac{\theta_1}{\theta_2} = \sqrt[4]{\frac{d_1}{d_2}}.$$

In a set of observations by Féry ranging from 850° C. to 1450°

C., the temperatures recorded by the thermo-couple differed from those calculated from the Stefan-Boltzmann law by amounts varying from 0 to 1·85 per cent of the quantity measured, the error never being greater than 16° C.

In the *Féry spiral pyrometer* the thermo-couple is replaced by a compound spiral (Art. 190) about 3 mm. in diameter and 2 mm. wide, composed of platinum and silver, of the form shown in fig. 148. The spiral is fixed at its centre, and the free end carries a light aluminium pointer which moves over a dial on which the temperatures are marked. A small reflector is placed at the back of the spiral to reflect back on to the spiral any rays that may pass through its convolutions. The graduation of the instrument is accomplished by observations at the fusing temperatures of bodies whose melting-points are known, or by comparison with a standard thermometer.

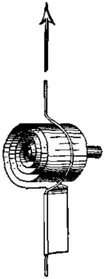

Fig. 148

197. The **Féry absorption pyrometer** is a photometric instrument, in which a comparison is made between the red rays emitted by a standard electric lamp, and the same rays emitted by a furnace or other hot body whose temperature it is desired to know. The radiation from the furnace passes through absorbing glasses which reduce its intensity to that of the lamp filament whose temperature is known. The coefficient of absorption of the glasses having been obtained for the wave length used, the required temperature is obtained.

A section of the instrument is shown in fig. 149. The tube OO′ is the telescope through which the hot body is seen. The rays from it pass through two glass wedges P, P′ to a lens O′ which brings them to a focus at the point G. At G is placed, at an angle of 45°, a glass plate silvered along a central strip. A side tube contains a standard lamp L, the rays from which are focused by a lens I on the silver strip at G. The rays from the given source pass through G, and those from the lamp are reflected from the strip on G, and both sets of rays are by means of a lens I′ brought to a focus and received in the eyepiece at O.

A piece of red glass *r* stops all the rays except the red, so that the eye sees a circle of red which, before the instrument is correctly adjusted, has a strip across it of different intensity. The adjustment

is effected by sliding the glass absorbing wedges P, P′ towards or from one another until equality in the two lights is produced; and the scale of temperature is carried by the pinion which moves these wedges. A, A are absorbing plates which, by reducing one or other of the two sets of rays in a known ratio, serve, when required, to vary the scale of the instrument. H is a screen that protects the eye from glare. This form of instrument is especially useful for measuring the temperatures of bodies that are small but very hot. At G′ is shown the appearance when a white-hot crucible is in the field of view simultaneously with the lamp.

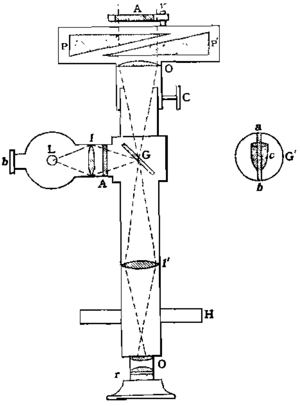

Fig. 149

The **Wanner pyrometer** is based on the same principle as that last described. The instrument selects from the rays emitted from the furnace those of a certain wave length, and compares them with the same rays emitted from a standard lamp. The selection of the rays in this instrument is effected by a direct-vision spectroscope. The rays are then polarized, and arrangements are made such that each set of rays forms half the field of view of the telescope. By means of an analyser the brightness of the more intense set of rays is reduced to that of the less intense, and the amount of rotation of the analyser serves to give the relation between the temperatures.

In the **Holborn-Kurlbaum pyrometer** a low-voltage incandescent electric lamp having a hairpin filament is placed in the focal plane of the objective of the telescope. The telescope is then turned towards the source, and an image of this is focused on to the filament of the

lamp. The current through the lamp is then adjusted till the filament becomes invisible on the background of the source (the temperatures being then the same), and its value is read on a milliammeter or sensitive galvanometer. The temperature of the filament is then deduced from the value of the current through it, which is read on a milliammeter in circuit with the lamp and its battery.

The connection between the temperature of the filament and the current is independently determined, the general relation being

$$C = a + \beta\tau + \gamma\tau^2$$

where τ is the temperature of the filament. Three measurements of C at known temperatures give the three constants. τ should not go beyond 1500° C. The lamps must be aged to get their permanent condition.

When the hot body whose temperature is required is not contained within an enclosure the walls of which are at the same temperature as itself, the reading obtained by a radiation pyrometer is too low. If the body have a lampblack surface the error is small, but with a mass of metal it may be 100 degrees or more. The amount of error varies according to the nature of the radiating surface. Holborn and Henning found that platinum emits only one-third and gold one-eighth of the red rays emitted by a black body at the same temperature, at their respective melting-points. According to Burgess, if θ_1 is the temperature of a black body and θ_2 that of a body which is of the same photometric brightness but is not black, then the following relation holds:—

$$\frac{1}{\theta_1} = \alpha \frac{1}{\theta_2} + \beta.$$

Thus when the constants α and β have been determined, the temperature of a body not black may be approximately obtained. For platinum, Lucas has found the values $\alpha = \cdot 9857$ and $\beta = \cdot 0000597$. According to these results, if we have a mass of platinum which is fully radiating and whose temperature is 1500° absolute, and a second mass of the same photometric brightness but is not enclosed in a chamber, then the temperature of the second mass is about 1640° absolute.

198. The work described in this article will illustrate the methods recently used for the determination of extreme temperatures, and the degree of accuracy attainable.

Four determinations of the *boiling-point* of sulphur, made by Rothe by means of mercurial thermometers having above the mercury, carbon dioxide under 20 atmospheres pressure, gave value 444·66°, 444·63°, 444·79°, and 444·82°. Measurements with a standardized thermo-junction gave a mean of 445°. Chappuis obtained the value 444·7°.

For *melting-points* up to about 1200° C. concordant results are obtained by different observers when the heating is done electrically and the temperature measured by a gas thermometer. Thus for the melting-point of gold Jacquerod obtained the value 1067°, Berthelot 1065·6°, and Holborn and Day 1064·3°. The method of Holborn and Day was to heat a large quantity of the metal in a crucible in an electric furnace whose temperature was measured by a thermocouple.

Another method was to take a piece of the metal in the form of a short thin wire, weld its ends to two thicker platinum wires, and join these wires in an electric circuit which also contained a current indicator. The metal under investigation was placed in a heating chamber side by side with a thermo-couple, and the temperature of the chamber was slowly raised until the metal fused, and broke the electric circuit. The indications of the thermo-couple just before the breaking of the current gave the temperature.

In another method a suitable metal block was placed in a heating chamber, and small fragments (about ·1 grm.) of the substance whose melting-point was required were dropped on the block. The lowest temperature at which the substance melted immediately on touching the block was taken as the melting-point.

In order to determine the melting-point of platinum, Harker wound a spiral of nickel wire on a cylinder of hard porcelain. By means of a current of electricity through the wire the temperature of the cylinder was maintained at about 1000° C. Inside this cylinder was placed a second tube, made of the materials of which the filaments of Nernst lamps are composed, which conduct electricity when hot. A current passed through the inner Nernst tube raised it to a very high temperature, and provided in its interior a hot chamber in which, by varying the current, any temperature up to approximately 2000° C. could be maintained. In this chamber was placed a thermo-electric couple made of a platinum wire and a platinum-iridium wire, and another composed of platinum and platinum-rhodium. The cold ends of the wires were connected to a suitable potential-measuring instrument, and the readings of the instrument

recorded at points between 400° C. and 1250° C., the temperature of the hot chamber being recorded by other independent means during this stage of the operations. From these observations was deduced a formula showing the variation of the electromotive force of the thermo-couples with the temperature. The temperature of the inner chamber was then raised until the melting of the platinum wire broke the electric circuit of the thermo-couples. The value of the E.M.F. recorded just before the fracture, inserted in the formula previously obtained, gave the melting-point of the platinum. The value thus deduced was 1710° C. (The melting-points of the platinum alloys are higher than that of pure platinum.)

By a similar method, using thermo-couples of platinum-rhodium, platinum-iridium, and iridium-rubidium, Waidner and Burgess obtained values between 1706° and 1731° for the melting-point of platinum, and from 1530° to 1543° for that of palladium.

Petavel determined the candle-power of the light emitted from a strip of hot platinum at various moderate temperatures, which he measured by methods previously described. Within those limits he found that the intrinsic brilliancy, or candle-power per square centimetre b, was connected with the temperature by the formula

$$\tau = 400 + 889{\cdot}6\sqrt[6{\cdot}9]{b}.$$

Heating the platinum to melting-point, he found that the value of b at this temperature was 19. Then the melting-point of platinum is $400 + 889\sqrt[6{\cdot}9]{19} = 1763°$ C.

Waidner and Burgess have recently made several determinations of high melting-points by means of the radiation pyrometer. In one set of experiments the furnace that contained the metal to be melted was made of iridium and was electrically heated, its structure being *such that the interior could be regarded as a "black body" to which* the laws of full radiation apply. The first stage was to compare the indications of a gas thermometer with those of ten thermo-couples at the melting-points of zinc (419° C.), antimony (630° C.), and copper (1084° C.), these melting-points being taken as already established. From these observations the laws of the thermo-couples and their constants were determined. Then by means of the thermo-couples they calibrated the lamp of a Holborn-Kurlbaum pyrometer, and verified the relation between the temperature (τ) of the lamp *filament and the current (C) passing through it*—

$$C = a + \beta\tau + \gamma\tau^2,$$

and determined the constants α, β, and γ. Thus they could calculate the temperature of the lamp at any degree of brightness. Then turning the radiation pyrometer on to the interior of the furnace in which the metal was melting, they compared its brightness with that of the lamp whose temperature was known. The temperature of the furnace was then calculated by Wien's formula connecting the relative temperatures of two sources emitting monochromatic radiation of different intensities.

They found the melting-point of platinum to be 1753° C. They also determined the melting-points of palladium as 1546° C., tantalum 2910° C., and tungsten 3080° C.

In another series of experiments Burgess stretched a thin strip of platinum in a blackened brass cylinder which was filled with pure hydrogen. On the strip was placed a very small piece of metal, and the strip was heated by an electric current. In the cylinder was a mica window by means of which the piece of metal was observed. At the moment when viewed through a telescope the metal was seen to melt, temperature observations were taken by a Holborn-Kurlbaum pyrometer. For iron in different states the values of the melting-point varied from 1499° to 1507°; cobalt, 1464°; nickel, 1435°; chromium, 1488°.

Employing practically the same method, but replacing the platinum strip by a Nernst glower, Mendenhall made the melting-point of rhodium 1907° and of iridium 2292°. Wartenberg, using the Wanner pyrometer standardized by taking as known the melting-point of gold, and using the Wien-Planck formula, made the melting-point of tungsten between 2800° C. and 2850° C.

To estimate temperatures such as those at which many of the metals boil, a radiation pyrometer is the only instrument available. Greenwood, using a Wanner pyrometer, made the boiling-point of copper 2310° C. Moissan, using a current of 300 amp. at 110 volts, distilled 300 grm. of copper in five minutes, and determined the temperature of vaporization as 2100° C. The distillation of gold required a current of 500 amp., and the temperature was determined as 2530° C. under atmospheric pressure. Moissan has also succeeded in distilling titanium at a temperature which was determined as 3500° C. This last temperature was that of the electric arc. Waidner and Burgess have also measured the temperature of the electric arc. Using a le Chatelier pyrometer, they obtained the value 3450° C.; a Wanner instrument gave 3410° C., and a Holborn-Kurlbaum instrument 3420° C.

Temperature of the Sun.—By comparing the energy of the radiation from the sun with that proceeding from some hot body whose temperature is known, the temperature of the surface of the sun is calculable by Stefan's law. The results obtained vary from 6200° A. (absolute) to 7000° A. As calculated by Wien's law, the temperature of the sun comes out about 5500° A.; but the sun may not be a full radiator, and the application of the law would therefore give a value below the actual temperature.

199. For the determination of very low temperatures, Dewar and Onnes have generally employed the hydrogen thermometer or a thermo-couple. From 273° A. to 173° A., Onnes made much use of a constantan-iron couple. For temperatures much below this, Dewar used couples of various metals and alloys. The couples are usually graduated by comparison with a hydrogen thermometer at three points, and the three constants thus obtained give a formula which is extended to lower temperatures. In one set of experiments to determine the temperature of boiling hydrogen Dewar used a thermo-couple of platinum and German silver. Its indications gave the temperature as 14·5° A., the hydrogen-gas thermometer recording 14·3° A. In another set, resistance thermometers gave: platinum, 34° A.; gold, 24° A.; and platinum-rhodium, 43° A.; and the constant-volume hydrogen thermometer, 21° A. These figures illustrate the divergencies and difficulties of determinations of such low temperatures.

200. The only rational theory of temperature measurement is that indicated in Chap. XXVI. The nearest practical approach to theoretical perfection is attained by the gas thermometer. For investigations that include a wide range of temperature the hydrogen thermometer is best used throughout, but its use needs great skill at very low temperatures.

Measurements of extreme temperatures made by pyrometers, by the specific-heat method, and by the electric methods are to be regarded as approximations only, and this for two reasons. The variable quantity on which their indications depend has been generally determined by experiments in which another thermometer was used, while the extension of the law of change of the variable beyond the limits within which it has been determined is very likely to introduce further error.

201. EXAMPLE.

The scale of a mercury thermometer agrees with the absolute scale at 0°, 100°, and 200° C., but reads ·1° too high at 50° C. Assuming that the deviation (D)

from the true scale expressed in degrees Centigrade can be represented by a cubic formula of the type

$$D = a\tau + b\tau^2 + c\tau^3$$

where τ is the reading of the mercurial thermometer, find the coefficients a, b, and c, and calculate the value of D for 500° C.

$$a\tau + b\tau^2 + c\tau^3 = D;$$

$$\therefore\ 100a + 10000b + 1000000c = 0 \ldots\ldots (1)$$

$$\text{also } 200a + 40000b + 8000000c = 0 \ldots\ldots (2)$$

$$\textit{also } 50a + 2500b + 125000c = \cdot 1 \ldots\ldots (3)$$

$$\text{From (1) and (2) } 200000b + 6000000c = 0.$$

$$\text{From (1) and (3) } 5000b + 750000c = -\cdot 2.$$

$$\therefore\ c = \cdot 000000266,$$

$$\text{and } b = -\cdot 0000798,$$

$$\text{and by substitution } a = \cdot 00532;$$

then for 500°

$$\begin{aligned} D &= \cdot 00532(500) - \cdot 0000798(500)^2 + \cdot 000000266(500)^3 \\ &= 2\cdot 6 - 19\cdot 9 + 33\cdot 2 \\ &= 14\cdot 9^\circ. \end{aligned}$$

QUESTIONS AND EXERCISES

1. What is an air thermometer? How is it constructed? and how is it used? What means have we besides the air thermometer of measuring temperatures between 400° and 800° C.?
2. A mass of copper weighing 6 lb. is taken from a furnace and placed in 20 lb. of water at 10°. If their final common temperature is 25°, find the temperature of the furnace. [Specific heat of copper, ·095.]
3. A weight thermometer filled with mercury at 0° C. weighs 302 grm., the vessel itself weighing 86 grm. The thermometer is then placed in a hot bath, when 4 grm. of mercury are expelled. Find the temperature of the bath.
4. Give some account of the precautions which must be adopted to make it possible to regard temperatures given by the mercurial thermometer as accurate to a few thousandths of a degree.
5. Discuss the relative advantages of the constant-volume and constant-pressure types of gas thermometer, and enumerate the principal sources of error.
6. Explain how the readings of a thermo-couple may be reduced to the scale of a gas thermometer by means of comparisons made at a limited number of selected points.
7. Describe the recent advances made in the methods of mercurial and electrical thermometry.

Part II
Principles of Thermodynamics

CHAPTER XVIII

WORK AND ENERGY

202. Thermodynamics is the science that treats of the application of the principles of dynamics to thermal phenomena.

Heat, regarded apart from our sensations, is motion—a form of energy. It will add much to the clearness of this conception if the habit is acquired of equating quantities of energy expressed in various forms.

We give here, for the convenience of the student, those dynamical definitions which are necessary for our purpose.

The units of mass, length, and time have been already given.

203. VELOCITY.—Velocity is rate of motion. When a body is moving with a uniform speed the velocity is measured by the distance passed over in unit time. Hence

In *British* measure a body is moving with unit velocity when it is moving at the rate of *one foot per second.*

In *C.G.S.* measure the unit of velocity is that of a body which is moving at the rate of *one centimetre per second.*

All measurements of velocity should be expressed in feet per second or centimetres per second.

Thus 60 miles an hour is a velocity of 88 ft. per second, and 3 Km. per minute is 5000 cm. per second.

When a body is moving faster at one time than at another its

velocity is said to be variable, and the value at any instant is measured by the distance which would be passed over in unit time if the body retained throughout the unit time a uniform velocity equal to that which it possessed at the instant selected for consideration.

204. ACCELERATION.—When a heavy body falls from a height to the ground, it falls faster in each succeeding than in each preceding second. Its velocity is said to be accelerated. When a moving locomotive engine shuts off steam its velocity is gradually reduced; this is a case of retardation or negative acceleration. When such a change takes place at a uniform rate, the number of units of velocity added or subtracted per second is called the **acceleration**. Since the velocity is expressed as so many centimetres (or feet) per second, the acceleration, which is the change of velocity per second, is expressed as so many centimetres (or feet) per second per second. The acceleration of a body falling freely to the earth in England is about 32·2 ft. per second per second. This is equivalent to 981 cm. per second per second.

If in two minutes the velocity of a locomotive change from 60 Km. to 24 Km. per hour, then the diminution of velocity in 120 sec. is 3,600,000 cm. per second. Whence the negative acceleration is 30,000 cm. per second per second.

In *British* units a moving body possesses unit acceleration when its velocity undergoes a change of one foot per second.

In *C.G.S.* units a moving body possesses unit acceleration when its velocity undergoes a change of one centimetre per second.

205. MOMENTUM OR MASS-VELOCITY.—When one body A impinges on another body B which is free to move, the body B is set in motion. The quantity of motion communicated to B is taken from that previously possessed by A. This "quantity of motion" is not simply velocity, since it depends on the masses of the bodies. If the body A be caused to impinge at the same rate and under exactly the same circumstances on a third body C, whose mass is different from that of B, the velocities acquired by B and C will be different, the greater mass will have acquired the smaller velocity, and the smaller mass the greater velocity; but the product of the mass into the velocity will be the same in the two cases. This product is the quantity of motion, or, as it is usually called, the **mass-velocity** or **momentum**. If two unequal masses are moving

with the same velocity, their momentum is different. *The momentum of a moving body is the product of its mass and its velocity.*

Unit of Momentum.—A body has unit momentum when it is of unit mass and is moving with unit velocity, or when the product of its mass and velocity equals unity.

The *British* unit of momentum is that of a body whose mass is one pound moving with a velocity of one foot per second.

The *C.G.S.* unit of momentum is the momentum possessed by a body whose mass is one gramme moving with a velocity of one centimetre per second.

Thus the momentum of a body whose mass is 20 grm. moving with a velocity of 50 cm. per second is 1000 units.

The momentum of a body weighing 1 cwt. and moving with a velocity of 15 miles an hour (22 ft. per second) is $112 \times 22 = 2464$ units.

206. FORCE.—From the idea of momentum we proceed to that of force, the two ideas being in dynamics very closely connected. With the nature of Force we are not concerned; it is here simply regarded as *that which tends to produce motion in a body at rest, or to change the motion of a moving body either in direction or magnitude.*

Let us imagine 1 grm. of matter at rest in space screened from the attraction of other matter. Let a force act continuously on this mass for one second; it will impart to the mass a certain velocity. If the same force act on a mass of 2 grm. during one second it will give that mass a velocity half as great as in the first case, and so on. But the momentum produced by this force acting for one second is in all cases the same. If the force act on the mass for more than one second it will continue to add to the momentum of the body as long as it is acting. Since force is one of those quantities that are incapable of direct measurement, we therefore use momentum to measure force. If the mass be already in motion when the force begins to act on it, the effect resulting from the force applied is exactly the same as if the body were originally at rest. The momentum communicated will be in the direction in which this force acts, and such direction may or may not coincide with the direction of the original motion.

The measure of a force is the momentum the force produces in its own direction in unit time. The unit of force *is that force which, acting for unit time on a unit mass originally at rest, causes the mass to move with unit velocity, or acting on any mass for unit time gives the mass* unit momentum *in the direction of action of the force.*

The *British* unit of force is that force which, acting on a mass of one pound for one second, gives it a velocity of one foot per second: the name of this unit force is the *poundal*.

The *C.G.S.* unit of force is that force which, acting on a mass of one gramme for one second, gives it a velocity of one centimetre per second: the name of this unit force is the *dyne*.

13825 dynes = 1 poundal.

A megadyne is a million dynes.

Suppose an engine to start moving a train whose mass is 200,000 lb., and suppose after 10 sec. the velocity of motion of the train is 5 ft. per second, then the momentum of the train at the end of these 10 sec. is 5 × 200000 = 1000000 units, and the force exerted by the engine is therefore 1000000 ÷ 10 = 10000 poundals.

Since the most obvious force in our experience is that of gravity, forces are commonly compared with weights, and we speak of a force as equal to the weight of so many grammes or a certain number of pounds; but this method is practical rather than scientific. The connection between this *gravitation measure* and the *absolute measure* given above may be thus shown:—

Suppose unit mass to be held suspended in the air. A force due to gravitation is tending to pull the mass and the earth together, and if the body fall, it is set in motion by this force. When the motion has lasted one second the velocity acquired is g, and since the mass is unity the momentum is also g. Hence the force which acted on the body is g. The numerical value of g is not the same in different latitudes.

The velocity acquired in England by a body falling freely under the action of gravity is (very nearly)

in *British* units 32·2 ft. per second. Whence a force equal to the weight of one pound is 32·2 poundals.

in *C.G.S.* units 981 cm. per second. A force equal to the weight of one gramme is 981 dynes.

Forces stated in gravitation measure may be converted into absolute measure by multiplying by the value of g thus—

1 *pound* = g *poundals*. | 1 *gramme* = g *dynes*.

Pressure.—Suppose two equal forces to be acting in opposite directions in the same straight line towards any point. The result is a *pressure*. We often have to speak of the pressure of a gas; this means the value of the force on unit area, and is usually measured

in grammes weight per square centimetre or pounds weight per square foot.

Comparative measures are often simply expressed as the heights of columns of mercury in a barometer or manometer.

207. WORK.—The preceding remarks and definitions are principally useful to us here as leading up to the conception of work and energy, because thermodynamics treats of Heat as a form of energy.

Suppose a man to pull a brick from the ground to the top of a tower. He has done work. If the weight of the brick be doubled the work done is doubled; if the height of the tower be increased the work done is increased in the same proportion. In raising masses of matter the work done is equal to the product of the weight raised and the distance through which it is raised.

Gravitation Units of Work.—Thus, as commonly expressed in gravitation units, we have—

Weight Overcome.	Vertical Height.	Work Done.
1 pound.	1 foot.	1 foot-pound.
1 *ton.*	1 *foot.*	1 *foot-ton.*
1 gramme.	1 centimetre.	1 gramme-centimetre.
1 kilogramme.	1 metre.	1 kilogramme-metre.

To raise 100 lb. through 50 ft. is to do 5000 foot-pounds of work; to raise 50 grm. through 100 cm. is to do 5000 gramme-centimetres of work.

The above mode of expressing work done is that which occurs first in one's experience, and although work done against gravity is only a particular case, it illustrates the general principle that work is done when a certain force is overcome through a certain distance, and that the amount of work done is measured by the product of the force overcome by the distance through which its point of application has moved.

$$Work = Force \times Distance.$$

Absolute Units of Work.—*Unit work is done when unit force is overcome through unit distance.* The practical units of work given above involve the force of gravity. Since this force is of different value at different parts of the earth, so that a foot-pound of work when done in Edinburgh is not precisely the same as a foot-pound

done in London, for accurate measurements absolute units must be employed, which are the same everywhere.

The absolute *British* unit of work is the work done when a force of one poundal is overcome through a distance of one foot. This unit is called a *foot-poundal*. It is nearly equal to the work done in lifting a mass of half an ounce through a vertical distance of one foot.

The absolute *C.G.S.* unit of work is the work done when a force of one dyne is overcome through a distance of one centimetre. This unit is called an *erg*. It is nearly equal to the work done in lifting a mass of one milligramme through a vertical distance of one centimetre.

C.G.S. Units.		British Units.	
Gravitation Measure.	Absolute Measure.	Gravitation Measure.	Absolute Measure.
1 gramme-centimetre.	g ergs.	1 foot-pound.	g foot-poundals.
1 gramme-metre.	100 g ergs.	1 foot-ton.	2240 g foot-poundals.
1 kilogramme-metre.	100000 g ergs.	—	—

421390 *ergs* = 1 foot-poundal.

On account of the smallness of the erg a multiple called the *joule* is sometimes, especially in electrical work, employed instead—

$$1 \text{ joule} = 10 \text{ million ergs.}$$

Work done against Friction.—Suppose a horse to drag a load along a level road. The amount of work done is proportional to the mass moved and the roughness of the road, the combined effect of these constituting the resistance to the motion, which is equivalent to a direct pull against the horse. The resistance in this case is due to friction. Evidently the load could be pulled along by an arrangement in which a falling mass was connected to the load by means of a string passing over a pulley (fig. 150).

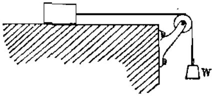

Fig 150

Hence the work done in this case may also be measured in gravitation units. The amount of work that must be expended to pull the mass W up again is equivalent to that done in dragging the load.

If the mass is dragged 30 ft., and the force of friction opposing the motion is equivalent to the weight of 70 lb., then the work done is 2100 foot-pounds.

If a body travels freely along a perfectly smooth horizontal table, no work is done. The force of gravity is acting on the body perpendicularly, but the motion is horizontal, and no work is therefore done against gravity, and friction is absent.

Friction is one of the most common modes by which mechanical energy is converted into heat.

Let A and B (fig. 151) represent two bodies with horizontal surfaces in contact. Then over the common surface and in a direction perpendicular to it there is a pressure or reaction w between the bodies. Let now a force f act on the body B in a direction parallel to the common surface, just sufficient to keep B in motion, then it is found by experiment that for the same two surfaces the ratio $\frac{f}{w}$ is constant. This ratio is here denoted by n, and is called the *coefficient of kinetical friction.* For ordinary substances, such as wood and metals, the value of n lies between ·15 and ·6. Suppose that for two metallic surfaces $n = \frac{1}{5}$, then this means that a mass B of one metal could be dragged over a horizontal surface of the other metal by a force acting horizontally and equal to one-fifth the weight of B. Since the work done is always equal to the product of the force by the distance through which the point of application of the force moves, writing s for the space through which the force f works in dragging a mass m along a rough horizontal plane, we have

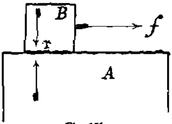

Fig. 151

$$w = mg$$
$$\therefore f = nmg$$
$$\therefore W = fs = nmgs$$

where W is the work done and g is the acceleration due to gravity.

The coefficient n for a railway train on the level varies from $\frac{1}{112}$ to $\frac{1}{180}$. Taking the former value, the work done in dragging a train whose mass is 300 tons through a distance of one mile is

$$W = \tfrac{300}{112} \times 2240 \times 32{\cdot}2 \times (1760 \times 3)$$
$$= 1020096000 \text{ foot-poundals.}$$

Work done on or by a Gas.—Suppose a quantity of gas enclosed in a cylinder in which a piston works. Let the pressure on unit

area of the piston be P and the area of the piston A. Suppose the gas to move the piston through a length l. Then the work done is $P \times A \times l$ units, which is equal to the product of the pressure (supposed constant) and the increase of volume.

If P is measured in	and V is measured in	then W is in
dynes per sq. cm.,	c.cm.,	ergs.
grammes per sq. cm.,	c.cm.,	centimetre-grammes.
lb. per sq. ft.,	c. ft.,	foot-pounds.

Thus if 1000 c.cm. of gas expands to 10000 c.cm. under a constant pressure of 10^6 dynes per sq. cm., the work done $= 9 \times 10^9$ ergs.

208. Graphical Representation of Work.—Since work is the product of force into distance, a quantity of work may be represented by an area by choosing as axes two lines at right angles to each other, and marking off a length along one axis to represent the force and a length along the other axis to represent the distance through which the force has worked.

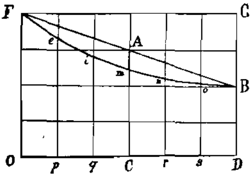

Fig. 152

The simplest case is that in which the force remains constant in value throughout the whole distance.

Thus, if in fig. 152 OF represent a force of 4 units working through a distance of 6 units represented by OD, then the work done is represented by the rectangle ODGF, whose area is 24 units.

If the force do not remain constant, but fall, at a uniform rate, *from 4 units to 2 units, then* OF *represents the force at the beginning* and DB its value at the end, and the area ODBAF represents the work done. The value of this area, 18 units, is obtained by multiplying the length OD by the ordinate CA, which represents the mean value of the force.

If the force diminish from 4 units to 2 units, but in a non-uniform manner, then the line which represents its changes ceases to be *straight, and the correct calculation of the area is less simple,* and often the construction of a figure on squared paper and the counting of the small squares included in the area is one of the readiest means of obtaining a fairly correct result for the work done.

Suppose it is known that the values of the force after six successive equal intervals are 3·33, 2·83, 2·42, 2·2, 2·1, and 2. Then setting up corresponding ordi-

nates *pe*, *qi*, &c., and drawing a curve through the points F, *e*, *i*, *m*, *n*, *o*, B thus obtained, the required area is marked out.

According to *Simpson's Rule* the area of such a figure may be obtained thus: Let the number of ordinates be odd; add together the first ordinate, the last ordinate, twice the sum of the other odd ordinates, and four times the sum of the *even ordinates*; *multiply the sum thus obtained by one-third of the common distance between the ordinates.*

According to this the above area is

$$\tfrac{1}{3} \times [4 + 2 + 2\{2\cdot83 + 2\cdot2\} + 4\{3\cdot33 + 2\cdot42 + 2\cdot1\}] = 15\cdot8.$$

For certain special cases the curve F*m*B is one of the regular forms, and the area can be correctly ascertained.

209. ENERGY.—*Energy is working capacity or the power of doing work*, and, like work, is measured in ergs or foot-poundals.

It requires an expenditure of work to set a mass of matter in motion, and the mass in coming to rest does an amount of work in some form or other exactly equal to that spent upon it.

Hence while the body was in motion it possessed the power of doing this work—i.e. it possessed energy. All moving bodies are by virtue of their motion endowed with energy, which, when it exists in this particular mode, is called **kinetic energy**.

If a mass is raised through a vertical height a certain amount of work is done upon the mass, and while it remains in its raised position it possesses an equivalent amount of energy. This energy of position is called **potential energy**. In all cases, if no energy has been dissipated, *the work done on a body is the measure of the energy communicated to it, whether the work has been spent in actually producing motion (kinetic energy) or in moving the body against the action of force into such a position that it is capable of doing work (potential energy).*

When a body is in the act of falling, its energy is changing from potential to kinetic. At the instant of reaching the ground all its potential energy has been converted into kinetic, and on striking the ground the kinetic energy of the moving mass is converted into heat—another form of energy. During the fall the total quantity of energy (kinetic + potential) remains constant; one increases just as much as the other decreases. A vibrating pendulum is an example of continual interchange of kinetic and potential energy.

Human operations consist in the transference of energy from one body to another.

Energy of a Moving Body.—Suppose a mass m to be raised through a height s, then the working force is gm, and the distance

being s feet, W the work done on the body is gms units. Therefore if the body be allowed to fall freely the energy possessed by the body at the instant of reaching the ground is gms units.

But it is known that when a body falls from a height s the velocity v acquired on reaching the ground is given by the equation

$$v^2 = 2gs,$$

$$\text{whence } s = \frac{v^2}{2g};$$

and, substituting this value for s in the above expression for the work done, we have

$$W = gm \times \frac{v^2}{2g} = \tfrac{1}{2}mv^2.$$

The expression $\frac{1}{2}mv^2$ is the value of the mechanical kinetic energy *of the mass m moving with a velocity v.*

This important result may be arrived at in a more general way. Thus, suppose a mass of matter to be at rest in space far beyond the reach of the attraction of any other matter. Let this mass be m grammes, and suppose a force of f dynes to act upon it for t seconds, producing in it a velocity of v centimetres per second, and during these t seconds suppose the body to have moved through s centimetres, then we have—

(i) Work done $= fs$ ergs.

(ii) Since the average velocity is $\frac{1}{2}v$ centimetres per second, and the time t seconds, therefore $s = \frac{1}{2}vt$.

(iii) Since the momentum produced in t seconds is mv, therefore the momentum produced in one second is $\frac{mv}{t}$, and this is equal to f, therefore $f = \frac{mv}{t}$.

Therefore the work done

$$W = fs = \frac{mv}{t} \times \tfrac{1}{2}vt = \tfrac{1}{2}mv^2.$$

As to the units it must be remembered that if we have

Mass m	Velocity v	then Energy $\frac{1}{2}mv^2$
in pounds,	in feet per second,	is in foot-poundals.
in grammes,	in centimetres per second,	is in ergs.

210. POWER.—Power is the *rate at which a machine or agent does work. It is measured by the number of units of work done in unit time.*

A **horse-power** is 550 foot-pounds per second.

A **watt** is the equivalent of the joule—i.e. 10^7 ergs per second; 1 watt = $\frac{1}{746}$ horse-power.

211. GENERAL PRINCIPLES OF THE SCIENCE OF ENERGY.—The principles of work and energy were originally derived from the study of machines. Practical mechanics, which preceded theoretical, was directed to the object of getting work out of machines. For many years much effort was expended in the attempt to discover perpetual motion—i.e. to find a machine that should work of itself, that should give out energy when none was supplied to it. All attempts failed, and these points gradually became clear—that a machine to which no energy is supplied can do no work; that a machine may multiply force but cannot multiply energy; and that the true function of a machine is to transmit work.

Work is the product of force by distance; and in proportion as a machine multiplies the force applied to it, it divides the distance through which the point of application of the force moves. Thus, if by a pulley a force equal to the weight of 1 lb. raises a mass of 8 lb. against the force of gravity, then the force must work through 8 ft. in order that the mass may be raised through 1 foot.

In driving a machine at least as much work must be done on it as can be obtained from it. Mechanical energy cannot be created. This is one aspect of the principle of the conservation of energy. All the simple machines are conservative, and therefore all complex machines are conservative also.

It was perceived, however, that in all machines there was an apparent *loss* of energy; no machine gives out as much work as is done upon it. This energy was for a long time supposed to be lost, but it was at last noticed that the *disappearance of mechanical energy is always accompanied by the production of heat.* If, then, heat were a form of energy, the principle of the indestructibility of energy would be made more probable. The experiments of Rumford and Davy (Art. 5) led independently to the suggestion that heat was molecular motion, and therefore a form of energy. The investigations of Joule turned the suggestion into a certainty by proving that *the heat developed when mechanical energy is destroyed is always exactly proportional to the energy that thus disappears.* Friction is the chief mode of converting mechanical energy into heat. To these considerations must be added the fact of the existence of heat engines such as the locomotive, the mechanical motion of which is wholly dependent upon the heat produced in the furnace. Heat thus is

proved to be a form of energy. But there are other forms also, and it is necessary here to allude to some of them. When a gun is fired a large quantity of energy is communicated to the shot, consequent upon the chemical actions that take place between the ingredients of the powder. As we have seen in Chap. XV, chemical action in general leads to a production of heat—i.e. of energy. Chemical affinity is therefore a form of energy.

If electrical currents be started in coils of wire suitably placed near each other, motion of the coils ensues, the energy of their motion being taken from that of the electric current. The coils also become heated by the passage of the current. An electrical current is therefore a form of energy. When a voltaic cell is used to produce the current, the origin of the energy is the chemical actions going on within the cell.

Without attempting a complete enumeration of the forms of energy we may note the following as the chief: mechanical energy, electrical energy, the energy of gravitation, heat, radiant energy, the energy of chemical affinity.

The science of energy embraces three great principles—

The Transmutation of Energy.
The Conservation of Energy.
The Degradation (or Dissipation) of Energy.

(i) **Transmutation of Energy.**

The first of these principles is that there are several forms of energy, and that energy may be converted from one form to another. From experiments such as those alluded to above, it appears that energy is readily capable of transmutation from the mechanical and electrical forms into the thermal form. In fact every kind of energy may be converted into heat. Other transmutations do not take place so readily as this. Many illustrations of transmutations of energy might be given. Thus the energy of a waterfall is sometimes employed to give motion to the armatures of dynamo machines by which it is converted into the energy of electrical currents, that may give out their energy either in the mechanical or thermal form many miles away. The tides may be thus utilized. Twice a day the sea rises round our coast, and if in falling it were made to turn water-wheels, a vast amount of work could be obtained.

A man may be regarded as a machine for transmuting the chemical energy contained in his food into mechanical work. He may work a treadmill which may turn the armature of a dynamo

machine and thus produce an electric current. It might be arranged that this electric current in passing through a wire should heat the wire, in which case the energy would have passed from the mechanical into the electrical, and from the electrical into the thermal form. In any case the chemical energy contained in his food maintains the heat of his body.

(ii) **Conservation of Energy.**

In these transmutations of energy none is destroyed. *Energy is alike indestructible and uncreatable* by any natural agency; the quantity of energy in the physical universe is absolutely fixed. This principle is not capable of simple direct proof, but "it is the one generalized statement that is found to be consistent with fact in all physical science" (Clerk-Maxwell). It was suggested by purely mechanical considerations, and was made more probable by the fact that when there was an apparent loss of energy in any machine heat was produced. The establishment of a numerical relation between the units of heat and of work by the methods to be described in the next chapter go far towards the establishment of the general principle, and many theoretical results deduced from it have been confirmed by observation.

(iii) **Degradation or Dissipation of Energy.**

The different forms in which energy can exist may be arranged in the order of their availability by us. Those at the top of such a list are called the higher forms, and those at the bottom the lower forms. Mechanical motion is one of the highest forms, and the heat contained in a body at low temperature is one of the lowest. Heat contained in a body at a high temperature is more available than heat contained in a body at a low temperature. When energy passes from a more available to a less available form, it is said to be degraded or dissipated.

Such transmutations of energy as those mentioned above cannot continue indefinitely. At each change the available energy grows less, because at each step of the process some of the energy runs down into the lower form of diffused heat. Thus, for example, we cannot convert all the energy of a waterfall into mechanical work, for the water running away possesses kinetic energy, which is gradually dissipated, i.e. it takes a form which we cannot employ for any useful purpose. We can always transform mechanical energy into heat, but this heat cannot be all transmitted back again into mechanical energy.

The chief means by which energy of motion is dissipated is

friction. Energy expended in friction generally becomes diffused, and, except by special means, cannot be recovered.

Since all our physical operations consist in transformations of energy, it would appear that when all the energy in the universe has run down to the lowest form all such operations must cease. The law of dissipation of energy may be thus stated: *Any transformation of energy is accompanied by a degradation of energy.* The more definite reasoning by which this principle is established with regard to heat engines is given in Art. 293.

212. EXAMPLES.

1. If a force equal to the weight of 10 lb. act upon a mass of 10 lb. for 10 sec., what will be the momentum acquired?

A force equal to the weight of 10 lb. acting on a mass of 10 lb. for 1 sec. gives to it a velocity of g ft. per second.

$$\therefore \text{ Velocity communicated in 10 sec.} = 10g \text{ ft. per second.}$$

The momentum acquired by the body is therefore $10g \times 10 = 100g$ units.

2. If the frictional resistance to a train is equivalent to 17 lb. per ton, what is the amount of work done against friction by a train of 150 tons in a journey of 10 miles?

$$\begin{aligned} \text{Resistance to motion} &= 17 \times 150 \text{ lb. weight.} \\ \text{Distance traversed} &= 52800 \text{ ft.} \\ \therefore \text{ Work done} &= 17 \times 150 \times 52800 \text{ foot-pounds} \\ &= 134640000 \text{ foot-pounds.} \end{aligned}$$

3. A mass of 10 lb. falls 100 ft., and is then brought to rest by penetrating 1 ft. into sand. Find the average pressure on the sand.

The total distance through which the mass falls before coming to rest is 101 ft.

Therefore the potential energy of the mass at the instant of starting is

$$\begin{aligned} 101 \times 10 &= 5 \times 1010 \text{ foot-pounds.} \\ \text{But this energy} &= fs \text{ and } s = 1. \\ \therefore f &= 1010 \text{ lb. weight.} \end{aligned}$$

4. A bullet of mass 1 oz. leaves the muzzle of a gun 3 ft. in length with a velocity of 1000 ft. per second. Find the average pressure of the powder on the bullet.

$$\begin{aligned} \text{Energy of the bullet} &= \tfrac{1}{2}mv^2 \\ &= \tfrac{1}{2} \times \tfrac{1}{16} \times (1000)^2 \\ &= 31250 \text{ foot-poundals.} \\ \text{But this energy} &= \text{work done by the powder} \\ &= \text{average force} \times \text{distance} \\ &= f \times 3 \\ \therefore 3f &= 31250 \\ \therefore f &= 10416{\cdot}6 \text{ poundals} \\ &= 323 \text{ lb. weight nearly.} \end{aligned}$$

EXERCISES

1. Find the number of ergs in 1 foot-ton, having given 1 lb. = 453·6 grm., 1 ft. = 30·48 cm., and 981 cm. per second per second as the acceleration due to gravity.
2. If the velocity of a body increase every second at the rate of 10 ft. per second, how should the acceleration be expressed if the units are 1 min. and 1 yd.?
3. Find the magnitude of the force which, acting on a mass of 3 kg. for 4½ sec., gives it a velocity of 23 m. per second.
4. Explain carefully what is meant by saying that a body is moving with an acceleration of 5, the units being feet and seconds.
5. A force f acting on a mass of 5 lb. increases its velocity in every second by 12 ft. a second; a second force f_1 acting on a mass of 28 lb. increases its velocity in every second by 7½ ft. a second; find the ratio of f to f_1.
6. Two bodies (A and B), weighing 10 lb. and 50 lb. respectively, are connected by a thread; B is placed on a smooth table and A hangs over the edge; when A has fallen 10 ft. what is the kinetic energy (or accumulated work) of the bodies jointly, and what of them severally?
7. How would these answers be affected if the table were rough and if the coefficient of friction between B and the table were 0·1?
8. Supposing the unit of force to be that force which acting upon 1 lb. for 1 sec. produces a velocity of 1 ft. per second; state the relation between the unit of force and the weight of 1 lb.
9. An engine weighing 50 tons moves for half an honr at a uniform rate of 30 miles an hour, the forces opposing its motion being equivalent to a weight of 15 lb. per ton weight of the engine. Find the work done.
10. How much work is done in raising 80 kg. through a vertical height of 50 m.? Give the answer in ergs.
11. A mass of 50 lb. is dragged along a rough horizontal plane for 10 min. at a velocity of 8 ft. per second. If the coefficient of friction is ⅓, find the work done.
12. How much work is done in bringing up the earth in boring a well 100 ft. deep and 10 sq. ft. in section if a cubic foot of earth weighs 3200 oz.? Give a diagram whose area represents the work done.
13. How much work is done in one stroke of a single-barrel air-pump if the area of the piston is 10 sq. in., length of stroke 6 in., pressure inside 17 in. of mercury at beginning and 16 at the end (varying uniformly), and pressure outside 30 in.?
14. A body, whose mass is 100 grm., is thrown vertically upwards with a velocity of 981 cm. per second. What is the energy of the bedy (1) at the moment of propulsion; (2) after ½ sec.; (3) after 1 sec.?
15. A shot of 1000 lb. moving at 1600 ft. per second strikes a fixed target. How far will the shot penetrate the target exerting upon it an average pressure equal to the weight of 12000 tons?
16. A cannon-shot of 1000 lb. strikes directly a target with a velocity of 1500 ft. per second and comes to rest; what is the measure of the impulse?
17. What is the horse-power of an engine which can project 10000 lb. of water per minute with a velocity of 80 ft. per second, 20 per cent of the whole *work done by the engine being wasted by friction, &c.?*

18. A body weighing 3 kg. (g = 980 cm.-sec.) and resting on a rough horizontal surface, requires a weight of at least 200 grm. connected with it by a thread over a pulley, and hanging vertically downwards, to make it move. Suppose the same body to be free (that is, not to have the weight attached to it) and to be moving with a velocity of 10 m. per second, how far will it continue to move on the rough plane before coming to rest?
19. A body weighing 10 lb. is placed on a horizontal plane, and is made to slide over a distance of 50 ft. by a force equal to the weight of 4 lb.; what number of units of work is done by the force? If the coefficient of friction between the body and the plane is 0·3, what number of units of work is done against friction? At the instant the 50 ft. have been described, what is there in the state of the body to show that the former exceeds the latter?
20. A man carries 2 c. ft. of cork up a hill 1000 ft. high. Find the work done by the air in raising the cork.
21. It has been asserted that there is a tendency for energy to become dissipated as heat. Discuss this statement, and give reasons for your conclusions with regard to it.

CHAPTER XIX

THE MECHANICAL EQUIVALENT OF HEAT

213. The mechanical equivalent of heat is the number of units of work that are equivalent to one unit of heat. It is generally called Joule's equivalent, after the great experimenter who determined its value, and is denoted by the letter J. Several methods have been employed in its evaluation. A known quantity of mechanical energy is converted into heat either directly or through some intermediate form, and the heat produced is measured in calories. The quantity sought is the ratio between the number of units of work expended, and the number of units of heat produced.

214. *FRICTION METHOD.*—The most satisfactory early results were obtained from the friction of water and other fluids.

Joule's Determination.—Joule's apparatus is shown in fig. 153.

A thin cylinder B of copper was filled with water and placed on a wooden stand. Inside the cylinder rotated a brass paddle-wheel having eight vanes, while fastened to the circumference of the vessel B were four vanes with spaces cut out just large enough to allow the rotating vanes to pass through. A horizontal section of the cylinder and vanes is shown at A, and a vertical section is shown at D, where the black portions represent the vanes of the paddle-wheel, and the shaded portions represent the vanes projecting from

the vessel's sides. This arrangement ensured that the vanes of the paddle-wheel when in motion did not carry the water round in front of them, but forced their way through it.

The paddle-wheel was set in motion by weights W and W′, which, by turning the axles of the pulleys P and P′, communicated motion to a roller R by means of the cords C and C′.

To render the loss of energy as small as possible the axles of P and P′ rested on friction wheels indicated at *ff*. The roller R was

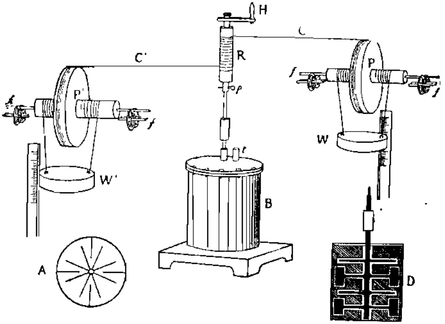

Fig. 153

connected with the axis of the paddle-wheel by means of a pin *p*, and could be disconnected therefrom, so that the weights could be wound up by the handle H without turning the paddle-wheel in the calorimeter. A delicate thermometer passing through an aperture *t* enabled the temperature of the water in B to be read to $\frac{1}{360}$ degree C.

In one particular experiment the mass of the weights W, W′ was 26318·2 grm. (nearly 60 lb.), the distance of their fall was 160·05 cm. (about 64 in.), and they were allowed to fall 20 times. Then the work done by the falling weights is

$$W = 20 \times 160{\cdot}05 \times 26318{\cdot}2$$
$$= 84244558 \text{ gramme-centimetres.}$$

The water-equivalent of the calorimeter B and its contents was

6315·97 grm. (about 14 lb.), and the rise of temperature recorded by the thermometer was ·3129° C.

Therefore the heat produced

$$H = 6315{\cdot}97 \times {\cdot}3129$$
$$= 1977{\cdot}27 \text{ calories.}$$
$$\text{Whence } J = \frac{84244650}{1977{\cdot}27} = \begin{cases} 42609 \text{ in gramme-centimetres} \\ \text{per calorie.} \end{cases}$$

Special experiments were made to ascertain the corrections necessary to be applied to this result.

(i) *For radiation;* the method is exemplified in Art. 167 on the laws of cooling.

(ii) *For friction of the axles.* The amount of work done in turning the paddle when there was no fluid inside B (with the same velocity as that acquired by it in the actual experiment) was determined by placing small weights in the place of W and W′.

(iii) For the *energy spent in the impact* of the weights with the floor and in the rebound.

(iv) For *vibrations* produced in the apparatus.

Elaborate care was taken to determine the effect due to these various causes. The corrected result for the above particular experiment was 42394 gramme-centimetres. The final result adopted by Joule from the whole of these experiments was that one calorie is equivalent to 42400 gramme-centimetres, i.e. 41·6 million ergs. In British units one pound-degree-Centigrade is equivalent to 1390 foot-pounds. Joule employed the same method with different substances, e.g. using mercury instead of water in the calorimeter. The value obtained for J was very close to that given above, showing that it was independent of the substances employed.

He also measured the heat developed by friction and the work done when water was forced through capillary tubes. This method gave a value for J almost exactly the same as that obtained by the method above described.

Rowland's Determination.—In 1879 Professor H. A. Rowland of Baltimore published an account of an elaborate repetition of these experiments. He was led to repeat them by these considerations. Joule experimented on water of one temperature only, assuming, on the authority of Regnault, that the specific heat of water was constant (see Art. 70), an assumption which required testing. Moreover, Joule did not reduce his temperatures to the readings of the air thermometer, and although his mercury thermometers were made

and graduated with extreme care, experience shows that the readings of such thermometers must be received with caution. Thirdly, the value of the specific heat of brass used by Joule in calculating the water-equivalent of his calorimeter was too high. And lastly, the rise of temperature obtained by Joule in his experiments was small, so that any error in reading would bear a considerable ratio to the whole change and largely affect the result.

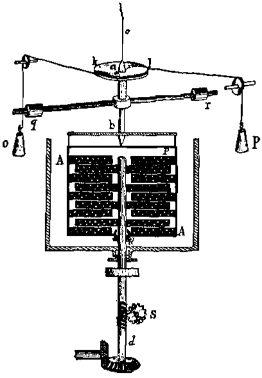

Fig. 154

Rowland therefore devised an apparatus on a much larger scale. An engine was employed to turn the paddles; each experiment lasted from 30 to 60 minutes; the calorimeter held 8·75 kg. (20·3 lb.) of water; and the rise of temperature obtained in the various determinations was from 15° to 25° C. The essential portions of the apparatus are indicated in fig. 154. The calorimeter AA and its accessories were fastened to an axle *ab*, which was suspended by a cord *c*. The paddle-wheel was connected with a shaft *dd*, which passed out at the bottom of the calorimeter, and which terminated in a bevelled wheel connected with a shaft driven by a belt from the engine. The number of revolutions of the paddle-wheel was registered by a counter S, which was turned by a screw on the shaft *d*. The paddle-wheel consisted of thirty-two small vanes affixed to the central axis in four horizontal rows, which passed between five similar rows of ten vanes, each fixed to the circumference of the calorimeter. All these vanes were pierced with numerous circular holes. The axle *ab* carried a wheel *kl* to the circumference of which, by means of tapes that passed over pulleys, the weights *op* were suspended. The shaft *ab* also carried a long arm supporting masses *q*, *r*, by means of which the moment of inertia of the calorimeter and its accessories could be adjusted.

When the paddle-wheel revolved the calorimeter tended to rotate; this tendency was balanced by the pull of the weights *op*. The moment of the force tending to turn the calorimeter was known from M the sum of the weights *o*, *p*, and the diameter (D) of the torsion wheel *kl*. The work W done when the paddles made N revolutions was equal to πNMD.

The calorimeter was surrounded with a water jacket, polished inside, and corrections were made for radiation. The results, which were very concordant at the same temperature, were as follows:—

Temp.	Value of J.	Temp	Value of J.
5°	$4{\cdot}212 \times 10^7$ ergs.	20°	$4{\cdot}179 \times 10^7$ ergs.
10°	$4{\cdot}200 \times 10^7$,,	25°	$4{\cdot}173 \times 10^7$,,
15°	$4{\cdot}189 \times 10^7$,,	29°	$4{\cdot}170 \times 10^7$,,
		35°	$4{\cdot}173 \times 10^7$,,

It will be seen that the value obtained for J diminishes as the temperature rises from 5° to 29°, and then increases. Rowland's conclusion was that this effect must be ascribed to variation in the specific heat of water, which, according to these experiments, has a minimum value at about 30° C.—a conclusion which more recent work appears to place beyond doubt.

215. ELECTRICAL METHODS.—It follows from the definitions of the absolute electrical units that when a quantity Q of electricity passes between two points whose difference of potential is E, the work W = QE ergs. And in the case of a uniform current C flowing for time *t* through a wire of resistance *r*

$$W = C^2rt \text{ ergs.}$$

The passage of the current through the wire produces heat; let H be the number of heat units (calories) thus produced. Then assuming that the energy of the electrical current expended in the conductor is the equivalent of the heat produced in it, we have—

$$J = \frac{W}{H} = \frac{C^2rt}{H}.$$

Continuous Current.—To determine J by this method it is thus necessary to pass a current of electricity of known value through a wire of known resistance for a certain definite time, and to ascertain the rise of temperature that takes place in a known mass of

water or other liquid in which the wire is immersed. The arrangement of the circuit is indicated in fig. 91, a battery, a standard galvanometer, the values of whose indications are accurately known in absolute units, and the wire wherein the heating effect is to be observed, being placed in series. Fig. 155 shows a common laboratory form of calorimeter somewhat resembling Joule's. The wire A is fastened to thick terminals, which are connected with the binding screws *d*, *d*, which are joined up to the wires *a*, *a* in fig. 91. Through the wooden lid of the calorimeter also pass a thermometer *b* and the rod of a stirrer *e*. In Joule's apparatus the wire A was of platinum-silver, in length about 4 yd., bent back on itself like the coils of a resistance box, and fastened to a glass tube, the whole being coated with shellac varnish. Its resistance was ·9895 British Association unit. The vessel F was of copper, and contained about a gallon of distilled water. It was supported on a wooden frame and carefully protected from draughts, and to diminish radiation it was surrounded with a layer of silk. Joule's stirrer was driven by clockwork.

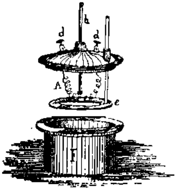

Fig. 155

In each experiment the current was allowed to pass for one hour, and the corrections to be applied for loss of heat from the calorimeter during that period by radiation and conduction were obtained by special experiments.

We give the details of one experiment.

The current C was ·3073 absolute C.G.S. unit. The resistance R was 989530000 absolute units. The time *t* was 3600 seconds, whence the electrical energy evolved was

$$W = C^2Rt = (\cdot 3073)^2 \times 98953 \times 36 \times 10^6$$
$$= 33639 \times 10^7 \text{ ergs.}$$

The water-equivalent of the calorimeter and its contents was 6081·96 grm., and the rise of temperature 1·312° C. Whence the heat H = 6081·96 × 1·312 = 7979·53 calories;

$$\therefore J = \frac{W}{H} = \frac{33639 \times 10^7}{7979 \cdot 53} = 42 \cdot 16 \times 10^6.$$

The final result obtained by this method differed by about 1 per

cent from the value obtained by the frictional method, and the discrepancy caused Joule to repeat the frictional experiments, with the result that their accuracy was still further established. The earlier results obtained by the electrical method were not entirely satisfactory, but recent more accurate determinations show no discrepancy with the results obtained by friction.

Transient Currents.—Joule also employed induced currents. If a metal wire (or mass) be moved so as to cut the lines of force in a magnetic field, transient currents are set up in the wire, and an expenditure of mechanical force is necessary to maintain the motion of the wire over and above that which would be necessary to maintain it if no magnetic field were present. The energy of the electric currents produced is the measure of this additional mechanical work.

Joule's arrangements were as follows:—

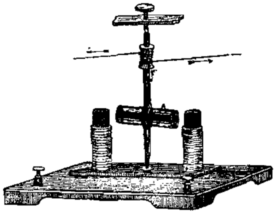
Fig. 156

A number of strips of soft iron, having oiled paper between them, were bound together. Round this core was wound a closed coil of silk-covered copper wire, and the coil was placed in a glass tube A, fig. 156, which was filled up with water, and mounted on pivots so that it could be rotated. One pole of a strong electromagnet being placed on each side of A, the rotation of the coil took place in a strong magnetic field, and an induced current passed round the coil every semi-revolution. The energy of the currents thus produced was converted into heat which warmed the wire, water, glass, paper, and iron. The rotation of the coil was produced by the fall of weights, the rotation being maintained for 15 minutes. The rise of temperature of the water in A gave the means of determining the heat produced. Corrections were made—

(i) For radiation as before.

(ii) For the heating of the water by its shaking about, and by conduction from the pivots on which the rotating coil was mounted. The amount of this was found by rotating the tube with the circuit of the electromagnet broken, and subtracting the rise in temperature

thus produced from the rise when the electromagnet circuit was made.

(iii) For the heat developed in the iron core within the coil by induced currents. The amount of this was found by repeating the experiment with the circuit of the inside coil broken.

(iv) For the energy required to maintain, when no inductive action took place, the velocity of rotation actually obtained in the experiment.

The result gave for the equivalent of a calorie 45·1 million ergs, a result considerably higher than that given by the frictional experiments.

In later experiments made on this principle by Violle, a disk of metal was caused to rotate between the poles of a powerful electromagnet. Powerful electric currents were produced in the disk, which therefore became hot, while, at the same time, the reactions set up rendered the disk difficult to turn. The heat produced in the disk is the equivalent of the mechanical energy expended in turning it. The rotation of the disk was produced by falling weights as in Joule's experiments; the heat produced was measured by rapidly transferring the disk after each operation to water in a calorimeter. After correcting for the various sources of error, Violle obtained the value 42·7 million ergs as the equivalent of the calorie.

216. METHODS FROM EXPERIMENTS ON GASES.—It is shown in Arts. 253 and 239 that when a mass of gas is compressed heat is evolved, and, conversely, that when such a mass expands heat is absorbed. Joule made use of methods founded on these principles.

(*a*) **Work done in Compressing a Gas.**—The principle of this method is to expend a known amount of work in compressing air in a reservoir, and to find the quantity of heat produced during the compression from the rise in temperature of a mass of water in which the reservoir is immersed.

In fig. 157 R represents a copper reservoir of 2237 c.cm. (about 144 c. in.) capacity standing in a vessel of water D. Into this reservoir air was compressed by the pump C. The entering air passed first through a tube G containing calcium chloride in order that any moisture present might be removed, then through a leaden spiral immersed in water contained in a vessel W in order that it might take a known temperature read by the very delicate thermometer t_1, then through a tube A into the reservoir R. The calorimeter D, which was of tinned iron, had double walls with an air

space between to check loss of heat by radiation, and the temperature of the water in it could be read very accurately by the thermometer t_2. The thermometers t_1 and t_2 at the beginning of the experiment gave the same reading—the temperature of the room. About 300 strokes were then made with the pump until the pressure

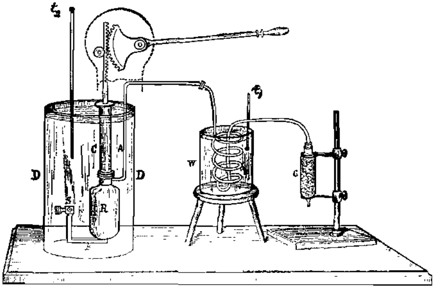

Fig. 157

in R had risen to 22 atmospheres, when the pump was stopped and the temperature of the water noted. Then we have—

Work done.—A volume V_1 of air at pressure P_1 (atmospheric) compressed at an approximately constant temperature to a volume V_2 (that of the reservoir R) whence $W = P_1V_1 \log_e \frac{V_1}{V_2}$. (See Art. 252.)

Heat produced when x grammes of water are raised through $y°$ C. $= xy$ gramme-degrees,

$$\therefore J = \frac{W}{H} = \left(P_1V_1 \log_e \frac{V_1}{V_2}\right) \div xy.$$

Corrections.—Heat was produced by the friction of the pump. The correction for this was calculated by working the piston 300 times without compressing air, and subtracting the rise in temperature due to this cause from the original reading.

The correction for radiation was made by the ordinary method.

In a particular experiment the following values were obtained: $P_1 = 1049$ grm. per sq. cm., $V_1 = 23482$ c.cm., $V_2 = 2237$ c.cm., $xy = 1325$ gramme-degrees. Whence

$$W = 1049 \times 23482 \times 2{\cdot}3026 \times \log_{10} \frac{23482}{2237}$$
$$= 56700000 \times \log_{10} 10{\cdot}49$$
$$= 56700000 \times 1{\cdot}02077$$
$$= 57878000 \text{ gramme-centimetres,}$$
$$\text{and } H = 1325 \text{ gramme-degrees;}$$
$$\therefore J = \frac{57878000}{1325} = 43700 \text{ gramme-centimetres.}$$
$$= 42{\cdot}9 \times 10^6 \text{ ergs.}$$

(*b*) **Work done during the Expansion of a Gas.**—When a gas expands, driving back the atmosphere, it does work in raising the atmosphere (Art. 239), and when the pressure of the atmosphere is known, the work done thereby is calculable. In doing this work an equivalent amount of heat disappears, which is abstracted from neighbouring bodies.

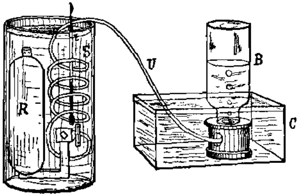

Fig. 158

Compressed air was contained in a reservoir R (fig. 158), and when a stopcock was turned passed through a spiral S and a tube U into the bottom of a vessel B containing water, and standing inverted in a larger vessel of water C. The reservoir R and spiral S were immersed in a known mass of water, the temperature of which was read at the beginning and at the end of the experiment by a delicate thermometer *t*.

The following are the results of one experiment:—

Work done by the Gas.—A volume of 44621 c.cm. of water was driven from B against an atmospheric pressure of 1040·5 grm. per square centimetre. Hence work done

$$W = 44621 \times 1040{\cdot}5$$
$$= 46428150{\cdot}5 \text{ gramme-centimetres.}$$

Heat absorbed.—The heat absorbed was that given out by 10682 grm. of water surrounding R in cooling through ·09666° C. Whence

$$H = 10682 \times \cdot 09666$$
$$= 1032 \cdot 52 \text{ calories,}$$
$$\therefore J = \frac{W}{H} = \frac{464281505}{10325 \cdot 2} = 44992 \text{ grm.-cm.}$$
$$= 43 \cdot 7 \times 10^6 \text{ ergs.}$$

217. METHOD FROM WORK DONE BY A STEAM ENGINE.—Hirn has attempted by experiments on steam engines to obtain a value of J by the converse process in which heat is converted into work.

(i) He measured the quantity and the pressure of the steam that passed into the cylinders of his engine in a given time. From these data were obtained the number of units of heat H_1 that passed into the cylinders.

(ii) He ascertained the amount H_2 of heat which was not converted into work, but which remained in the steam when it entered the condenser of the engine, by causing it to warm a known quantity of cold water through an observed range of temperature.

The difference $H_1 - H_2$ represented the heat-equivalent of the work done by the engine.

(iii) The work W done by the engine was measured in dynamical units by means of an indicator diagram (Art. 279).

Such measurements do not admit of a high degree of accuracy, but in his latest series Hirn obtained a mean value for J differing very little from that obtained by Joule.

218. RECENT DETERMINATIONS.—Many careful evaluations of the mechanical equivalent of heat have since been made.

Griffiths employed the electrical method. The calorimeter containing the wire and the water to be heated was closed by an air-tight lid, and was suspended in an enclosure which had double walls, the space between them being filled with mercury. The formula $JH = C^2rt$ in Art. 133 may be written $JH = \frac{E^2t}{r}$ where E is the difference of electrical potential between the terminals of the wire whose resistance is r. Griffiths kept E constant by means of a regulating rheostat, and measured E by balancing it against a number of Clark standard cells in series. The mercury thermometer employed was standardized in terms of the hydrogen

scale. The temperature range was between 15° C. and 25° C., and his final value was 4·192 joules per calorie.

Messrs. Schuster and Gannon also employed the electrical method, writing the equation in the form JH = CE*t*. The value of the current C was ascertained from the quantity of silver deposited in a silver voltameter, and E was measured by balancing against 20 Clark cells in series. Their result at 19° C. was 4·191 joules per calorie.

The experiments of Callendar and Barnes, described in some detail in Art. 76, furnish one of the most accurate measurements of the value of J. Using their latest value for the electromotive force of the Clark cell (1·433 volt), their value for the mean calorie is 4·185 joules.

Employing the friction method, Messrs. Reynolds and Moorby made some experiments on a large scale for the determination of the mean value of J between 0° C. and 100° C. They employed a steam engine of 100 h.p. fitted with a hydraulic brake which consisted of paddles working in a vessel of water. The water flowed into the vessel at about 0° C. and out at about 100° C. Their final value for the mean calorie was 4·183 joules.

219. **Summary of Results.**—The values obtained for J by the various experimenters and methods are:—

	Method.	Temperature C.	Value of J.		
			Foot-pounds per 1° F.	Foot-pounds per 1° C.	Ergs per 1° C.
Joule (final)	Friction	15°	772·6	1390	$4·155 \times 10^7$
Rowland	Friction	5° to 35°	777·6	1399	$4·185 \times 10^7$
Griffiths	Electrical	15° to 25°	779	1401	$4·194 \times 10^7$
Schuster and Gannon	Electrical	—	779	1401	$4·194 \times 10^7$
Reynolds and Moorby	Friction	0° to 100°	777	1398	$4·183 \times 10^7$
Callendar and Barnes	Electrical	—	777·6	1399	$4·185 \times 10^7$
Barnes	Electrical	5° to 35°	777	1398	$4·183 \times 10^7$
Miculescu	Friction	10° to 13°	776·6	1398	$4·180 \times 10^7$
Cremieu and Rispail	—	—	777·6	1399	$4·185 \times 10^7$
Mean of Modern Values ...	...	...	777	1398	$4·183 \times 10^7$

It is now generally held that Joule's value is too low; the discrepancy being probably due to differences in the thermometers.

220. The measurement of the mechanical equivalent of heat, both by the frictional and the electrical methods, is now an ordinary laboratory experiment.

Friction.—A form of apparatus devised by Callendar is shown in fig. 159. The calorimeter consists of a cylindrical vessel made of thin metal. This is mounted on a horizontal shaft and is surrounded by a silk belt, to the ends of which unequal weights are attached in the manner of a friction brake. The cylinder is rotated by hand or by a motor, and the *heat developed by* the friction of the belt upon the cylinder is communicated to a known mass of water within it, whose rise in temperature is ascertained by a thermometer inserted axially within it. The weights are adjusted to balance the friction of the belt, and a spring balance which carries a portion of the smaller weight takes up the result of inequalities and makes the arrangement stable. A counter geared to the shaft registers the number of turns made by the cylinder. The method of calculating the result is given in Art. 214.

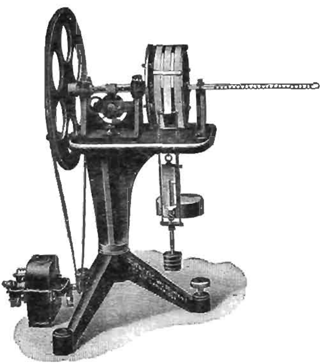

Fig. 159

Electrical.—The apparatus shown in fig. 160 is a simplified form of that employed by Callendar and Barnes (Chap. VII). The energy is supplied by a steady battery K, which sends a current round a helix of manganin wire N. The value of the current is measured by an ammeter L, and the difference of potential between the ends of the wire N by a voltmeter G. The wire N is contained within a long glass tube along which a stream of water is passed, entering by a tube Q and leaving through a tube D. The temperature of the

water on entering and leaving the tube is measured by two thermometers T′, T. A special form of cistern B is used to maintain the flow of water constant. It consists of two concentric cylinders. Into the outer annular compartment water flows from a supply pipe P at such a rate as to run over into the inner compartment and away through a waste pipe F. The outer compartment is thus always kept full to a certain height. The tall tubes AA serve to take off bubbles of air. The adjustments having been made by

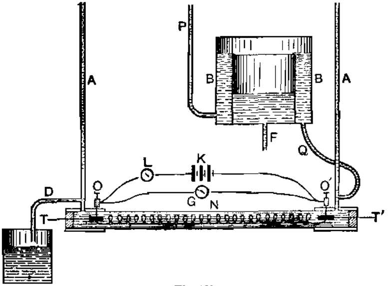

Fig. 160

previous trials, the current is turned on and the water is set flowing. The issuing water is caught in a vessel, and the mass that passes in a time t ascertained. Then if C is the current and E the voltage,

$$CEt = JH.$$

Also, if m is the mass of water that passes, and τ_1, τ_2 the readings of the thermometers,

$$H = m(\tau_2 - \tau_1),$$

$$\therefore J = \frac{CEt}{m(\tau_2 - \tau_1)}.$$

221. FIRST LAW OF THERMODYNAMICS.—The results of the important experiments described in this chapter are summed up in the first law of Thermodynamics, which may be thus enunciated:—

"*When work is transformed into heat or heat into work the quantity*

of work is mechanically equivalent to the quantity of heat" (Clerk-Maxwell). Symbolically expressed

$$W = JH.$$

It has been proposed to call the amount of heat which is equivalent to one *erg* of mechanical energy a *therm*. If then mechanical energy be expressed in ergs and heat in therms the equation becomes

$$W = H.$$

This most important law is the expression of the principle of the Conservation of Energy as applied to thermal phenomena.

It was by the application of this principle that Lord Kelvin discovered the phenomena of the electric convection of heat (Art. 138). His argument was as follows: Consider a copper-iron circuit with one junction at their neutral temperature (about 270°) and the other at some lower temperature. A current flows from copper to iron through the hot junction, and may be made to do work. To provide this energy heat must disappear somewhere in the circuit. None disappears at the hot junction, for at that temperature the metals are neutral to each other and there is no difference of electrical potential between them. And at the cold junction there is known to be, by Peltier's principle, an evolution of heat. Therefore the thermal energy required to maintain the current must be absorhed in the copper or iron wires themselves, i.e. either a current in iron from the hot to the cold portion must cool the iron, or a current in copper from cold to hot must cool the copper, or both these results must follow. The mode by which the effects were experimentally determined has been given.

222. EXAMPLES.

1. If the standard substance were iron (specific heat, 0·114), what would be the value of J?

$$J = \frac{\text{Unit of work}}{\text{Unit of heat}}.$$

The unit of work is independent of any particular substance; the value assigned to J is therefore simply inversely proportional to the unit of heat. If iron were used instead of water in defining the unit of heat, this unit would be diminished in the ratio of 1000 to 114, the ratio of their thermal capacities, and the value of J would therefore be increased in the same ratio.

$$J_1 = J \times \frac{1000}{114}.$$

2. A cylindrical calorimeter of outside diameter 20 cm. is suspended by a single wire so that it is capable of rotation about its vertical axis. A paddle

is rotated within the calorimeter at the rate of 1500 turns per minute, and the calorimeter is kept from rotating by means of two fine strings, which are wound round the outside of the calorimeter on opposite sides and then pass over two pulleys, and have each a weight of 200 grm. attached. If the mechanical equivalent of heat is $4{\cdot}189 \times 10^7$, and g is 981, find the heat developed in the calorimeter per second.

$$\begin{aligned} \text{By Art. 195 W} &= \pi\text{NMD per second} \\ &= 3{\cdot}1416 \times 25 \times 400 \times 20 \\ &= 628320 \text{ grm.-cm. per second}; \\ \therefore \text{H} &= 628320 \div \left(\frac{4{\cdot}189 \times 10^7}{981}\right) \\ &= 14{\cdot}7 \text{ calories per second.} \end{aligned}$$

3. Taking $4{\cdot}2 \times 10^7$ as the numerical expression of the mechanical equivalent of heat in the C.G.S. system and the Centigrade scale of temperature, find its value when the second, milligram, millimetre, and 1° F. are the units.

$$4{\cdot}2 \times 10^7 \text{ ergs} = 1 \text{ grm.-deg. C.}$$

$$\therefore 4{\cdot}2 \times 10^7 \times \frac{1}{981} \times \frac{5}{9} \text{ grm.-cm.} = 1 \text{ grm.-deg. F.}$$

$$\therefore 4{\cdot}2 \times 10^7 \times \frac{1}{981} \times \frac{5}{9} \times 10 \text{ grm.-mm.} = 1 \text{ grm.-deg. F.}$$

Since the gramme appears on both sides of this equation, the change to milligram would merely multiply both sides by 1000 and leave the relation unaffected. Hence in the given units

$$\text{J} = \frac{21 \times 10^8}{981 \times 9} = 23{\cdot}4 \times 10^5.$$

4. A lead bullet strikes a steel target with a velocity of 500 ft. per second. Find the rise of temperature produced in the bullet by the impact, supposing all the energy to be converted into heat within the bullet. (Specific heat of lead = ·0314.)

The question is independent of the mass of the bullet, which may be therefore taken as unity.

(1) Kinetic energy $= \frac{1}{2}mv^2$

$$\begin{aligned} &= \tfrac{1}{2} \times 250000 = 125000 \text{ foot-poundals}; \\ \therefore \text{H} &= \frac{125000}{32{\cdot}2 \times 1390} \text{ pound-degrees.} \end{aligned}$$

(2) Let x = rise of temperature of bullet; then heat absorbed $= x \times {\cdot}0314$ units.

$$\begin{aligned} \therefore x \times {\cdot}0314 &= \frac{12500}{32{\cdot}2 \times 139} \\ \therefore x &= \frac{12500}{32{\cdot}2 \times 139 \times {\cdot}0314} \\ &= 88{\cdot}9°. \end{aligned}$$

5. A windmill works at 4 horse-power for 24 hours, and 90 per cent of the work done is stored up as energy. Of this energy 90 per cent is employed in

heating water from 12° C. to the boiling-point. How many pounds of water will be so heated?

One h.p. = 33000 foot-pounds per minute.

∴ Total work done = $33000 \times 4 \times 60 \times 24$ foot-pounds.

∴ Energy expended in heating water

$= 33 \times (24)^2 \times 10^4 \times \cdot 81$ foot-pounds

$= 33 \times (24)^2 \times 10^2 \times 81 \div 1390$ pound-degrees of heat.

To raise 1 lb. of water from 12° C. to 100° C. requires 88 pound-degrees.

$$\therefore \text{ Number of pounds heated } = \frac{33 \times 24 \times 24 \times 81 \times 100}{1390 \times 88}$$
$$= \frac{9 \times 24 \times 810}{139}$$
$$= 1258 \cdot 7.$$

6. A hole is punched through a wrought-iron plate 1·2 cm. thick, the mean pressure on the punch being equal to the weight of 30000 kg. If one-fifth of the whole work done is spent in heating the part punched out, which weighs 150 grm., find its rise of temperature.

(Specific heat of iron = ·11.)

(i) Work done by force equal to the weight of 30000 kg. working through 1·2 cm.

$= 30000 \times 1000 \times 1 \cdot 2$ grm.-cm.

$= 36 \times 10^6 \times 981$ ergs.

∴ *Mechanical energy converted into heat*

$= 7 \cdot 2 \times 10^6 \times 981$ ergs,

$= 7 \cdot 2 \times 10^6 \times 981 \div 42 \times 10^6$ calories,

$= 7 \cdot 2 \times 981 \div 42.$

(ii) *Number of heat units absorbed by the iron if x = rise of temperature in degrees C.*

$= 150 \times x \times \cdot 11$

$= 16 \cdot 5x$ calories.

$\therefore 16 \cdot 5\, x = 1 \cdot 2 \times 981 \div 7$

$\therefore x = (1 \cdot 2 \times 981) \div (7 \times 16 \cdot 5)$

$= 10 \cdot 2°$ C. nearly.

7. A specimen of coal contains 80 per cent of carbon and 4 per cent of hydrogen uncombined with oxygen. How many gramme-degrees of heat are generated by the combustion of one gramme of this coal; and with what velocity must a gramme of matter move that the energy of its motion may be equal to the energy developed by burning the gramme of coal?

(The combustion of one gramme of carbon produces 8000 grm.-degrees, and the combustion of one gramme of hydrogen produces 34000 grm.-degrees.)

One gramme of coal contains $\frac{4}{5}$ grm. of carbon and $\frac{1}{25}$ grm. of hydrogen.

∴ Heat produced $= \frac{4}{5}$ of $8000 + \frac{1}{25}$ of 34000 calories

$= 7760$ calories

$= 7760 \times 42 \times 10^6$ ergs.

The energy of one gramme of matter, moving with a velocity of v cm. per second, $= \frac{1}{2}v^2$ ergs.

$$\therefore v^2 = 2 \times 7760 \times 42 \times 10^6$$
$$= 4000 \sqrt{40740}$$
$$= 807200 \text{ cm. per second.}$$

QUESTIONS AND EXERCISES

1. Find in foot-pounds the difference between the energy of a pound of steam and a pound of water, both at 50° C.
2. Express in ergs the specific heat of air, and in foot-pounds the latent heat of steam at 100° C.
3. Two equal masses of water, moving with equal velocities in opposite directions, impinge on each other and are both brought to rest. The heat developed is sufficient to raise their temperatures from 0° C. to 1° C. Find their velocity in miles per hour.
4. A mass of 50 kg. falls from a height of 30 m. How much heat is produced in the impact with the ground, if the mass neither penetrates nor rebounds?
5. Find (*a*) the amount of heat necessary to raise 15 lb. of lead from a temperature of 115° C. to its melting-point 320°, and then to melt it; and (*b*) with what velocity the mass must be moving in order that the conversion of its energy of motion into heat may produce the required amount.
6. How many units of heat are produced when 1 ton of iron is dragged 100 ft. along a horizontal surface, the coefficient of friction being $\frac{1}{8}$?
7. A mass of platinum strikes an obstacle with a velocity of 500 ft. per second. Find the rise of temperature in the platinum produced by the impact, supposing half the heat developed to be employed in warming it. [Specific heat of platinum = ·0324.]
8. With what velocity must a pound of ice at −10° C. strike a target in order that it may be converted into water at 10° C., supposing that 80 per cent of the mechanical kinetic energy of the moving mass is converted into heat within the substance? [Sp. heat of ice = ·5; J = 1404.]
9. Water leaves a mill-wheel at the rate of 5 ft. per second. How much unused energy does this represent per ton of water that passes? If the fall of the water is 8 ft., what fraction of the whole energy is taken up by the mill, neglecting any initial velocity of the water?
10. A train of 200 tons travels 300 yd. from its start before acquiring its permanent velocity. If the accelerating force during that period is equal to the weight of 14 lb. per ton weight of the train, find how many units of heat would be developed if the train were pulled up.
11. An engine works at 4 h.p. for 24 hours, and 10 per cent of the work done is employed in melting ice at 0° C. How many pounds of ice will be melted?
12. A man is employed for an hour in turning an apparatus such as Joule's (Art. 195). If he work at the rate of 4×10^{10} ergs per minute, what rise of temperature would be produced in 10 kg. of water?
13. A steam engine driving a dynamo works at the rate of 10 h.p. The current from the dynamo drives a motor which does external work at the rate of 5000 watts. Find the percentage of energy dissipated; and its amount in calories per second.

14. Over a certain lamp 2 lb. of water originally at 15° C. is raised to boiling point in 20 min. If half the heat produced by the lamp is communicated to the water, compare the rate at which energy is being evolved from the lamp with the rate known as a horse-power.
15. An electric current is maintained in a circuit by a single Grove's cell. If half of the energy of the current is converted into heat within a calorimeter containing water, find to what temperature a kilogramme of water originally at 15° C. would be raised during the oxidation of 1 grm. of zinc in the cell.
16. The whole of the heat generated when 60 lb. of lead falls from a height of 695 ft. is used in melting ice. What weight of ice will be melted assuming that the temperature of the lead is 0° C. and $J = 1390$?
17. Dry ice at 0° C. is thrown into 20 lb. of water at 60° C. until the whole weighs 23 lb. How much mechanical work must be done on the water in order to heat it again to 60° C.?
18. How much mechanical work must be done on one hundredweight of mercury to raise its temperature from 10° C. to 20° C.?
19. How much warmer is the water at the bottom of the Niagara Falls than at the top? [Height of fall = 160 ft.]
20. Find the heat developed by the stoppage of a train of 300 tons, travelling at 50 miles an hour.
21. A leaden bullet falls 100 ft. and strikes the ground. Its temperature is raised 4·32° F. by the impact. Assuming that all the heat generated by the impact is communicated to the bullet, and that the specific heat of lead is ·03, calculate the mechanical equivalent of heat. Why is the method impracticable?
22. An engine consumes 40 lb. of coal, and during the process performs 16000000 foot-pounds of work. If the combustion of 1 lb. of the coal develop heat sufficient to convert 16 lb. of water at 100° C. into steam at the same temperature, what percentage of the heat produced in the engine is utilized?
23. If mechanical energy equivalent to 50000 foot-pounds is expended in warming 3 lb. of water at 10° C., to what temperature will it be raised?
24. With what velocity must a mass of sulphur at 15° C. strike a stone slab in order that the heat developed in the impact may melt the sulphur?
25. How much hydrogen must be burned in order to evolve sufficient energy to raise 1000 kg. through 1000 m. vertical height?
26. Find in pound-degrees-Fahrenheit the energy required to raise 1 ton through a height of 200 ft.
27. A boy can do 1200 foot-pounds of work per minute. If the work is applied in heating water, find how many pounds of water would be raised from 0° C. to 100° C. in half an hour.
28. From what height must a hailstone at 0° C. fall to the ground in order that it may be melted by the heat produced in the impact with the ground?
29. How far must a mass of mercury fall in order that its temperature may be raised 1° C.?
30. A locomotive engine consumes 160 lb. of carbon per hour, and converts 5 per cent of the heat evolved into mechanical energy. At what rate could the engine draw a train of 100 tons along a level line against a resistance of 10 lb. per ton?
31. In question 11 at the end of Chap. XVIII, if the mass be of iron, and half the work done is converted into heat within the mass, find the rise of temperature.

32. Find the ratio between the energy required to warm a pound of silver through 50° F. and that required to raise it through 2123 ft.

CHAPTER XX

THE KINETIC THEORY

223. MOLECULES, ATOMS, AND ELECTRONS.—The idea propounded by certain Greek philosophers that matter consists of small indivisible particles was revived by Daniel Bernouilli, for the purpose of explaining the "spring of the air", whose law was discovered by Boyle. It proved a good working hypothesis, explaining so much so well that it now ranks as a well-established theory, the evidence in its favour being drawn both from Chemistry and Physics. Dalton showed that the fact that elements unite in fixed proportions to form chemical compounds was readily explicable on the hypothesis that the compound resulted from a grouping together of particles, whose relative weights were multiples or submultiples of the proportions observed. These ultimate portions of a substance, which it is impossible by any physical process to subdivide, are called molecules. The *molecules of any particular substance are alike in nature, structure,* and mass, but the molecules of different substances differ in respect of these properties.

These molecules of ordinary matter are as a general rule not in actual contact. In gases the spaces between the molecules are much larger than the molecules themselves. Hence gases are very compressible; the process of compression is one of forcing the molecules closer together.

An important principle known as the law of Avogadro, which is supported by a mass of evidence, asserts that "*Equal volumes of all substances when in the state of gas, and under like conditions, contain the same number of molecules*".

Avogadro's law affords a ready explanation of the fact that the permanent gases follow the same laws of change of volume with change of temperature and pressure, as well as of the further fact that other gases tend also to obey the laws of Boyle and Charles as their gaseous condition approximates to that of the permanent gases.

In the case of compound substances it is generally possible by chemical or electrical means to break up the molecules into the par-

ticles of which they are composed, and which are called atoms; but *when this is done the original substance has ceased to exist, and two* or more different substances are produced. Thus each molecule of a compound substance is itself a group of atoms that act together as one system, the nature of the substance being determined by the atoms of which the molecule is composed. In some elementary substances the molecule consists of one atom only; in others, of two or more. The atoms of any particular element are all equally heavy and precisely alike. *But certain relations exist between the atomic* weights and other properties of elements, which suggested that the atoms themselves are built up of smaller masses of some common material. And the systems of bright spectral lines which the radiation from different elementary substances give, have also suggested that the atom itself is a more or less complicated system, the component parts of which possess vibratory or rotatory motions.

In 1879 Crookes discovered that when the pressure of the gas in a vacuum tube was reduced to about one-millionth of an atmosphere he obtained from the cathode a continuous discharge of rays, atoms, or particles which, besides producing various electrical and optical effects, were capable of turning a small wheel when directed upon one of its vanes. In 1897 J. J. Thomson showed that these cathode "rays" consisted of small corpuscles of matter carrying a negative *charge of electricity and moving with great velocity. And since* that date a whole class of "radioactive" substances has been discovered which all possess the property of shooting out from themselves small particles (called β particles) which possess the same characteristics as the corpuscles of the cathode discharge in a Crookes' tube. These corpuscles, called negative electrons, appear to be constituent parts of the atom. According to the **electron theory**, *each atom is a system containing positive and negative* electrons. The electrons are in motion, and are at least in some cases capable of detachment from the atom. Their independent motion produces thermal and electrical effects; their motion within the atom produces vibrations in the ether manifested by the spectral lines. And there is some evidence that by the expulsion of electrons from the atom the structure of the atom may be so changed that *a new elementary substance is formed.*

224. MOTION OF THE MOLECULES.—That the molecules of fluids possess a motion of translation is proved by the phenomenon of diffusion.

If a jar filled with gas be left open to the air, the gas disappears

from the jar. Let two wide-mouthed bottles be filled with different gases collected over water or mercury, their mouths closed with glass plates, and the jar containing the lighter gas be placed vertically over the other. Let the plates be removed, and after a short interval replaced. Then it is found that the contents of the two bottles are identical. Half the molecules of the lower gas have passed upward and half those of the upper gas downward. Every gas diffuses into every other gas in this way.

Graham's Law.—Graham found that gases diffused into each other when divided by a porous solid. Thus let a glass tube be stopped at one end by a disk of some kind of unglazed earthenware. The kind known as "biscuit ware" is generally used, the pores of this substance being very fine. Let the tube be filled with hydrogen and placed with its open end under water or mercury. The liquid rises in the tube, and after a time it is found that the gas in the tube is not hydrogen but air. The hydrogen has passed through the disk, aud a smaller volume of air has also passed through it in the opposite direction. Thus gases pass through the same porous body under the same conditions at different rates, as is shown by the difference between the volumes of the hydrogen that passed out of the tube and the air that passed into it. Graham found that *the rates of diffusion of gases are inversely proportional to the square roots of the densities of the gases.*

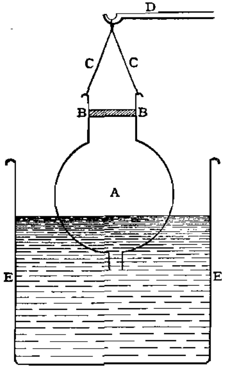

Fig. 161

This law may be verified by an apparatus such as that shown in fig. 161, where the tube is in the form of a "diffusion bulb" A. B represents the porous disk, and CC threads by which the bulb is suspended from one arm D of a balance. By this arrangement the position of the bulb can be so adjusted that the level of the liquid in the bulb is always the same as that in the vessel E, and complications that would be introduced by hydrostatic pressure are avoided.

The bulb is filled with hydrogen (or other gas), while the mouth above B is closed by an impervious stopper of indiarubber. When the bulb is adjusted in position this stopper is removed and diffusion through B begins. When liquid ceases to enter the bulb, the aperture at the bottom is closed, and the volume of water that has entered is measured. Hence the volume of the air (V_2) that has entered is known, and the volume of the hydrogen (V_1) that passed out is also known. The ratio V_1/V_2 is the ratio between the rates of diffusion of the gases. And it is found that

$$\frac{V_1}{V_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

where ρ_1 and ρ_2 are the densities of the gases.

The ratio between the volumes of the gases that passed through the plug gives the ratio between the velocities of their molecules. Hence the rates of motion of the molecules of different gases at the same temperature are inversely proportional to the square roots of their densities, the heavy molecules moving slower and the light molecules faster.

The rate of motion also depends on the temperature, temperature and rate of molecular motion increasing and decreasing together.

As the gaseous particles move to and fro frequent collisions or encounters occur between them. The length of the journey between any two encounters is called the **free path**. The denser the gas the shorter is the free path, the rarer the gas the longer the free path.

The free path under ordinary pressures is very short, but experiments by Tait and Dewar and by Crookes show that the free path in a very good "vacuum" may be several centimetres.

The encounters have the effect of constantly changing the direction of motion and the velocity of the molecules and of causing them to vibrate.

According to the calculations of Clerk-Maxwell the following are the values of the molecular constants for hydrogen under standard conditions of temperature and pressure:—

Number per cubic centimetre	2×10^{19}
Mass of molecule	$4{\cdot}5 \times 10^{-24}$ grm.
Distance between centres of molecules (average)	5×10^{-8} cm.
Length of mean free path	17×10^{-6} cm.

Other calculations made on different bases give figures of the same order of magnitude. Thus Lorentz makes the number of molecules

per cubic centimetre $3{\cdot}5 \times 10^{19}$, and Meyer gives the length of the mean free path as $18{\cdot}5 \times 10^{-6}$ cm.

In **liquids** the molecules move about in a manner similar to the motion in gases except that the free path does not exist, and the rate of motion is therefore much less.

In **solids** the molecules have no motion of translation, but execute vibrations or movements about a certain mean position.

225. MOLECULAR FORCES.—Between the molecules of a mass of gas under moderate pressure there is scarcely any trace of cohesion. One portion shows no tendency to remain contiguous *to another portion.* If the gas be greatly compressed, slight cohesion appears; it becomes much greater when the gas is liquefied, and much greater still when the substance has become solid. Thus when molecules are very close together there exists between them a great attractive force. *We obtain some idea of the distance within* which this force becomes sensible, by a study of liquid films and surfaces.

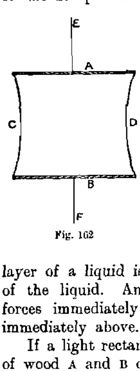

Fig. 162

Surface Tension.—*If a small quantity of* mercury be placed on a smooth table it gathers itself into a form more or less spherical. A *steel needle may be made to float on the surface of water,* but sinks rapidly when once the surface is penetrated. Thus the surface *layer of a liquid is in a condition different to that of the mass* of the liquid. And this is due to the fact that the molecular forces immediately below the surface are not the same as those immediately above.

If a light rectangular framework (fig. 162) made of two pieces of wood A and B connected by two pieces of cotton C and D be *dipped in soap solution, a film may be withdrawn from the liquid.* By means of threads EF the film may be pulled out till it is very thin. Force is required to pull out the film, and if the pull be relaxed the film contracts.

If a soap bubble be blown on the mouth of a funnel, and the open end held near a lighted candle, the film contracts and expels the air with such velocity that the candle may be blown out.

These and many similar phenomena prove that the surface layer of liquids behaves like an elastic membrane in tension. The tensile **force per centimetre** remains the same whatever the size and thick-

ness of the film may be, provided that the temperature is constant, thus showing that it is essentially a surface phenomenon, the layer of water between the two skins playing no part in the phenomenon.

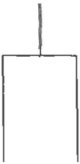

Fig. 163

If a piece of thin wire be bent into a framework of three sides as in fig. 163 and suspended from one arm of a balance so as to dip into water or soap solution, the tension of the film may be measured by weights placed in the other pan of the balance.

A more accurate method of finding the value of the surface tension is by measuring the ascent (or depression) of liquids in capillary tubes by means of a cathetometer as indicated in fig. 164, the level of the mass of liquid being taken

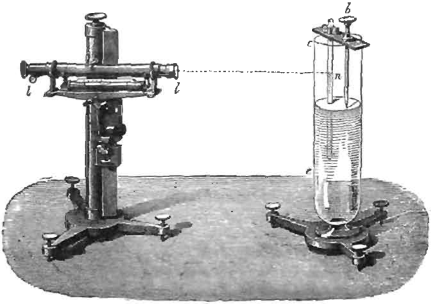

Fig. 164

as that of a point just touching the surface. The value of the surface tension is calculated thus:—

Let a = the radius of the tube,
f = the value of the surface tension in dynes per centimetre (lineal),
ϵ = the angle of contact between the liquid and the tube,
ρ = the density of the liquid,
h = the height of the liquid column,
g = the acceleration due to gravity;

then the force of gravitation on the column of liquid held up in the tube by the surface tension is

$$\pi a^2 h\rho g,$$

and the vertical force exercised by the surface tension of the film round the circle where it is in contact with the glass is

$$2\pi af \cos e.$$

$$\therefore\ 2\pi af \cos e = \pi a^2 h\rho g$$

$$\text{whence } f = \frac{ah\rho g}{2 \cos e},$$

and e being determined by a separate experiment, f is readily found. In the case of clean water in clean glass tubes $\cos e = 1$.

The value of f for a water-air surface is 81 dynes per centimetre, and is found to diminish with rise of temperature by rather more than $\frac{1}{500}$ of its value at 20° C. for each Centigrade degree. This variation may be ascertained within a moderate range by accurately measuring f on different occasions when the temperature of the laboratory is different, or by placing the vessel in fig. 164 in a bath.

The surface tension diminishes with rise of temperature because at higher temperatures the molecular motions are increased and the average distance between the molecules becomes greater.

At the critical temperature the surface tension of a liquid would become equal to that of its vapour, which may or may not be zero.

The thickness of the layer within which the surface tension resides gives some indication of the distance within which these molecular forces act.

If a film be formed within a rectangular framework of metal placed vertically, and viewed by white light, at first it is white all over. It consists of a film of water between two skins. As the liquid descends gradually to the bottom of the film under the influence of gravity, the film at the top gets thinner and horizontal bands of colour appear—green, blue, deep violet in succession. At a certain thickness the film becomes dark at the top, and careful observation shows that spots appear blacker than the rest. The film then breaks. The thickness of the black film as measured by Reinold and Rücker is about $1{\cdot}1 \times 10^{-6}$ cm., which is $\frac{1}{50}$ of the wave length of yellow light. Hence it appears that the molecular forces which produce cohesion come into play when the distance between the molecules is of the same order of magnitude as the wave-length of light.

226. PRESSURE OF A GAS.—If a billiard ball be shot

against the face of a disk behind which is a spring, the spring will be momentarily compressed. If the operation be repeated many times a second with equal force, the spring will remain permanently compressed and may be made to register a certain pressure.

A mass of gas consists of a vast number of molecules which at a definite temperature are moving with a certain determinate mean velocity. A vast number of knocks take place every second *against the sides of a vessel that contains a gas, and the result is a steady pressure.* If the mass of gas be compressed into a smaller volume and the rate of motion of the molecules remain unaltered, it is clear that a larger number of impacts upon the side of the vessel take place per second and the pressure upon it is accordingly increased. If the volume be increased the number of impacts per second is diminished and the pressure is diminished. The tendency of gases to expand is at once seen to result from the motion of the molecules.

In Art. 232 *it is shown more exactly how the velocity of motion* of the molecules is connected with the pressure of the gas

227. CONDUCTION OF HEAT.—Since the temperature of any portion of gas is decided by the velocity of motion of its molecules, as the molecules move about they must tend to equalize the temperature of different parts of the same mass. For as the molecules move to and fro and collide with each other, those that are moving faster gradually part with some of their energy of motion to *those that are moving more slowly. Heat is thus conducted from one part of a fluid to another.* In a solid the increased energy of motion has been supposed to pass from one molecule to another by radiation. But the effect may be due to the motions of the electrons.

228. EVAPORATION AND CONDENSATION.—The processes of evaporation of a liquid and condensation of a vapour are results of molecular motion. The velocities of motion of different molecules differ greatly in each state, but are on the average greater in the vapour than in the liquid. At any particular instant some *molecules of the liquid have a velocity greater than the average* velocity of the gaseous molecules, and these when moving towards the surface escape into the vapour. And, conversely, some gaseous molecules moving slowly towards the surface become entangled amid the molecules of the liquid, and their rate of motion is not sufficiently great to enable them to free themselves. These become liquid.

These converse processes of evaporation and condensation are always simultaneously proceeding. When a saturated vapour exists *in contact with its liquid the processes are proceeding at equal rates.*

229. CHANGE OF STATE.—Since the molecules of a solid have no motion of translation, while those of a liquid have such motion, when a solid is converted into a liquid an addition of molecular energy is acquired. This partly accounts for the latent heat of liquefaction. As the solution of a solid in a liquid is similarly a process of liquefaction, heat is similarly absorbed. When a liquid is converted into a gas, an additional quantity of motion is communicated to the molecules. This corresponds to the latent heat of vaporization.

230. VELOCITY OF MEAN SQUARE.—Since the molecules are in frequent collision their velocities undergo frequent change, and at any given moment the velocities have every possible value between a certain minimum and maximum. Hence to find an expression for the kinetic energy of millions of moving molecules a special method is adopted.

The motion of each molecule in the intervals between the encounters is considered to take place according to the laws of dynamics stated in Chap. XVIII. Thus if m be the mass of any molecule and v the velocity of its motion at any instant, its kinetic energy of translation is $\frac{1}{2}mv^2$. Now although for any individual molecule this quantity may be ever varying, yet its average amount per molecule in any fixed condition of the gas remains unchanged, since there are always many molecules in every possible phase of change.

Suppose, then, at any instant we have n particles each of mass m, but moving with different velocities v_1, v_2, v_3, &c. Then E, the sum of the kinetic energies, is the sum of the n terms $\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \frac{1}{2}mv_3^2$, &c.

$$\therefore \text{E} = \tfrac{1}{2}m(v_1^2 + v_2^2 + v_3^2 + \ldots\ldots\ldots\ldots v_n^2).$$

Now there must be some quantity $\bar{v}^2$ such that $n\bar{v}^2 = v_1^2 + v_2^2 + v_3^2 + \ldots v_n^2$. This quantity $\bar{v}^2$ is called the velocity of mean square of the moving particles.

For example, suppose 100 bodies each of mass m are in motion with respective velocities of 1, 2, 3, ... 100 ft. per second.

Then the sum of their kinetic energies is

$$\begin{aligned} \text{E} &= \tfrac{1}{2}m(1)^2 + \tfrac{1}{2}m(2)^2 +, \text{\&c.}\ldots\ldots\ldots\tfrac{1}{2}m(100)^2. \\ &= \tfrac{1}{2}m(1^2 + 2^2 + 3^2 +,\ldots\ldots\ldots 100^2). \\ &= \tfrac{1}{2}m\,\frac{100 \times 101 \times 201}{6}. \\ &= \tfrac{1}{2}m \times 338350. \\ &= \tfrac{1}{2}m(100)\,(58\cdot1)^2. \end{aligned}$$

Then $(58\cdot1)^2$ ft. per second is the velocity of mean square of these bodies.

So long as the condition of the gas remains unchanged, the value of $\bar{v}^2$ remains constant. Hence for the energy of a mass mn of gas, i.e. of n molecules each of mass m, we have

$$E = \tfrac{1}{2}mn\bar{v}^2.$$

231. KINETIC ENERGY OF UNIT VOLUME.—If n be taken as the number of particles in unit volume, mn represents the mass of unit volume—i.e. the density. Thus, writing ρ for the density,

$$E = \tfrac{1}{2}\rho\bar{v}^2.$$

If two such sets of moving particles be introduced into the same vessel, Maxwell proved that during the encounters they will exchange energy until finally the value of $\tfrac{1}{2}m\bar{v}^2$ is the same for each set of particles. When the average kinetic energy of each molecule is the same, there is no further passage of energy from one set to the other.

During the process, since mn is fixed there is only a change in the value of $\bar{v}^2$. This process corresponds to a passage of heat from one mass to the other, and the final condition represents a state of thermal equilibrium, when there is no tendency for heat to pass from one body to the other. The process is therefore an adjustment of temperatures, and the two volumes of gas are of equal temperature *when the kinetic energies of their molecules are of equal average* amounts per molecule. Whence it follows that the temperature *of the gas depends upon, and is some function of* $\bar{v}^2$.

232. VELOCITY OF MOLECULAR MOTION.—Consider a hollow centimetre cube containing gas at some definite temperature and pressure.

If all the n molecules are moving to and fro in parallel lines between two opposite faces of the cube, each with a velocity of v *centimetres per second, then the number of hits per second is* v *for* each molecule, and the total number is nv, viz. $\tfrac{1}{2}nv$ on each face. But at each impact the motion is entirely reversed, and there is therefore a change of momentum from mv to $-mv$, that is, a change of $2mv$ for each single impact of each molecule; the total change of momentum thus impressed on the mass of matter impinging on one face is $\tfrac{1}{2}nv \times 2mv = mnv^2$ per second. But the change of momentum produced in one second is the measure of the force—i.e. of the pressure on the plane (Art. 206). The pressure on the face is therefore mnv^2.

Now suppose all the molecules to be moving about indiscriminately in all directions and with velocities not the same. Then the motion of each can be resolved into three rectangular components, and it may be shown that the result will be as though one-third of the whole number passed straight between each pair of opposite faces, while in the place of v^2 we must write $\bar{v}^2$, and the expression for the pressure becomes

$$\begin{aligned} P &= \tfrac{1}{3}mn\bar{v}^2 \\ &= \tfrac{1}{3}\rho\bar{v}^2; \\ \text{or } \bar{v}^2 &= \frac{3P}{\rho}. \end{aligned}$$

Also it has been shown that $E = \tfrac{1}{2}\rho\bar{v}^2$;

$$\therefore E = \tfrac{3}{2}P.$$

The pressure exerted on unit area by any gas is equal to two-thirds of the kinetic energy of unit volume.

The expression also shows that equal volumes of all gases at the same pressure possess equal amounts of kinetic energy due to the motion of translation of the molecules.

Example.—A litre of hydrogen at 0° C. under a pressure of 1033·3 grm. per sq. cm. contains ·0896 grm. Find the velocity of mean square of the hydrogen particles, assuming $g = 981$.

Here $P = 1033{\cdot}3 \times 981$ and $\rho = {\cdot}0000896$

$$\begin{aligned} P &= \tfrac{1}{3}\rho\bar{v}^2 \\ \therefore 1033{\cdot}3 \times 981 &= \tfrac{1}{3} \times {\cdot}0000896 \times \bar{v}^2 \\ \therefore \bar{v}^2 &= \frac{10333 \times 981}{{\cdot}0002987} \\ &= \frac{10333 \times 981}{29870} \times 10^8 \\ \therefore \bar{v} &= 10^4\sqrt{\frac{10333 \times 981}{29870}} \\ &= 10^4\sqrt{339{\cdot}36} \\ &= 10^4 \times 18{\cdot}41 \\ &= 184100 \text{ cm. per second} \\ &= 6097 \text{ ft. per second.} \end{aligned}$$

The velocity of motion of the molecules of other gases may be obtained from this result by noting that the formula above shows it to be inversely as the square root of the density of the gas. Thus, for example, the velocity for oxygen is one-fourth of the above value.

233. EXPLANATION OF PHYSICAL LAWS. Boyle's Law.—If we now consider unit mass of a gas occupying a volume V

under pressure P, then the density $\rho = \frac{1}{V}$, and the equation $P = \frac{1}{3}\rho\bar{v}^2$ may be written in the form $PV = \frac{1}{3}\bar{v}^2$.

If then the value of $\bar{v}^2$ remain the same, i.e. the temperature be kept constant, the product PV remains invariable. This is **Boyle's Law.**

The fact that Boyle's law is not exactly obeyed by any gas shows that the motion of the molecules does not take place exactly as described above. In actual gases, when the molecules are very close together, molecular forces come into operation which modify the paths and periods of the molecules, and Boyle's law ceases to represent the connection between the volume and pressure of the substance. See Art. 225.

Further, if we take the experimental fact that in any given mass of gas the product $PV = R\theta$, i.e. PV is proportional to the absolute temperature of the gas, it follows from the above equation that $\theta \propto \bar{v}^2$.

Charles's Law.—From Art. 231 it follows that for two different gases in thermal equilibrium

$$\frac{1}{2}m_1\bar{v}_1^2 = \frac{1}{2}m_2\bar{v}_2^2;$$

and since for each gas $\theta \propto \bar{v}^2$, it follows that temperatures measured by different gases are proportional to one another, i.e. the rate of expansion of all gases is the same.

Rise of Temperature on Compression.—If the particles of gas are impinging on a piston in a cylinder with a certain velocity, and the piston is suddenly forced in, the velocities with which the particles rebound must be greater than before. The increased kinetic energy is rapidly distributed throughout the mass, and the value of $\bar{v}^2$ on which the temperature depends is increased accordingly.

Avogadro's Law.—It has been shown above that if we consider unit volume of any gas, the pressure $P = \frac{1}{3}mn\bar{v}^2$. Thus for unit volume of two different gases at the same pressure and temperature

$$P = \frac{1}{3}m_1n_1\bar{v}_1^2 = \frac{1}{3}m_2n_2\bar{v}_2^2.$$

If communication be established between these two masses of gas no change of temperature results, and hence no change takes place in the values of $\bar{v}_1$ and $\bar{v}_2$. But in such a mixture it has been shown that finally $\frac{1}{2}m_1\bar{v}_1^2 = \frac{1}{2}m_2\bar{v}_2^2$ (Art. 231). From these equations it follows that

$$n_1 = n_2.$$

All gases under the same pressure have the same number of molecules in unit volume.

Graham's Law.—Again, since for unit volumes of two different gases at the same pressure and temperature

$$3P = m_1 n_1 \bar{v}_1^2 = m_2 n_2 \bar{v}_2^2$$

$$\therefore \frac{\bar{v}_1^2}{\bar{v}_2^2} = \frac{m_2 n_2}{m_1 n_1} = \frac{\rho_2}{\rho_1}.$$

The molecular velocities are inversely proportional to the square roots of the densities of the gases.

Dulong and Petit's Law of Atomic Heats.—As applied to the simple gases this law has now acquired a clear meaning. Regnault's results given in Art. 77 show that these gases possess the same specific heat for unit volume, and it has now been shown that they possess the same number of molecules in unit volume; whence it follows that their molecules have precisely the same thermal capacity. Since almost every substance assumes the form of an almost perfect gas at a certain temperature, the equality of the atomic heats of many of the solid elements shown in the table on p. 87 suggest the wider conclusion that the atoms of all simple substances have the same capacity for heat.

234. MOLECULAR VIBRATIONS.—In addition to the motion of translation, the molecules have a vibratory motion which goes on simultaneously with the motion of translation. In the case of compound molecules there is reason to think that the atoms composing them have also their respective special movements. A portion of the total energy of a molecule is due to the movements of its constituent parts.

Thus when a mass of a solid is heated *in vacuo*, although but little external work is done these effects are produced—

(*a*) *The temperature rises, a process which involves an increase* of molecular kinetic energy.

(*b*) The substance changes volume, a process that usually involves an expenditure of energy in overcoming inter-molecular forces, i.e. forces that exist between the molecules of the substance.

(*c*) Energy may be absorbed in effecting intra-molecular changes, i.e. changes in the vibrations or relative positions of the atoms that constitute the molecule.

Confining our attention to gases a definite result may be obtained. It has already been shown that a difference exists between the

specific heat of a gas at constant volume and that at constant pressure, the difference being due to external work done in the latter case (Art. 239). But when a gas is heated under such conditions *that no external work is done the effect is still complex. The energy* expended has increased not only the motion of translation of the molecules, but also done work *within* the molecules themselves in driving their atoms farther apart, in causing these atoms to vibrate faster, &c.

To take an example. Suppose a centimetre cube of oxygen to be heated from 0° C. to 1° C. at constant volume. The specific heat of oxygen at constant volume is known by direct experiment to be about ·155, and the mass of 1 c.cm. at 0° C. is ·0014107 grm. Thus *the energy necessary to raise 1 c.cm. of oxygen from 0° to 1° without expansion is*

$$\begin{aligned} H &= \cdot 0014107 \times \cdot 155 \text{ calorie.} \\ E &= \cdot 0014107 \times \cdot 155 \times 42 \times 10^6 \text{ ergs.} \\ &= 9183{\cdot}7 \text{ ergs.} \end{aligned}$$

Now, it has been shown above that the kinetic energy E due to the motion of translation of the particles of a gas is $\frac{3}{2}$ P. Therefore the increase of E, which we will call $dE = \frac{3}{2}\,dP$ where dP is the corresponding increase of pressure. If the original pressure was that of the atmosphere, *viz.* $1{\cdot}014 \times 10^6$ dynes, per sq. cm.,

$$\begin{aligned} \text{then } dP &= \frac{1{\cdot}014 \times 10^6}{273} \text{ dynes,} \\ \text{and } dE &= \tfrac{3}{2} \times \tfrac{1}{273} \times 1014000 \text{ ergs} \\ &= 5571{\cdot}4 \text{ ergs.} \end{aligned}$$

Thus it appears that the energy of the cubic centimetre of gas has been increased by 9183·7 ergs, of which only 5571·4 ergs are accounted for by the increased kinetic energy of translation of the molecules.

The difference 3612·3 ergs is the energy that has been expended in doing work within the molecules themselves. The ratio between the whole energy and the energy of agitation concerned in the operation is

$$\frac{H}{dE} = \frac{91837}{55714} = 1{\cdot}65.$$

This ratio, which is usually written β, has nearly the same value for all the more perfect gases.

235. As appears from the above example in general symbols

$$dP = \frac{P}{\theta}$$

$$\therefore dE = \tfrac{3}{2}\frac{P}{\theta}$$

$$\text{and } H = \tfrac{3}{2}\beta\frac{P}{\theta}.$$

If we deal with unit mass instead of unit volume this equation must be multiplied by the specific volume V, i.e. the number of units of volume in unit mass. The left-hand side then becomes K_v, the specific heat at constant volume, and we have

$$K_v = \tfrac{3}{2}\beta\frac{PV}{\theta}.$$

Here β and $\frac{PV}{\theta}$ are constant, and the expression shows that the specific heat of a gas at constant volume is an invariable quantity whatever the pressure and temperature may be.

236. RATIO OF SPECIFIC HEATS.—From the above expression for K_v, a value of γ, the ratio between the specific heats may be found (see Chap. XXIII).

$$\text{For } K_p = K_v + \frac{PV}{\theta} \text{ (Art. 239)}$$

$$\text{but } K_v = \tfrac{3}{2}\beta\frac{PV}{\theta}$$

$$\therefore K_p = \frac{PV}{\theta}(\tfrac{3}{2}\beta + 1)$$

$$\therefore \gamma = \frac{K_p}{K_v} = \frac{\tfrac{3}{2}\beta + 1}{\tfrac{3}{2}\beta} = 1 + \frac{2}{3\beta}.$$

Substituting the value 1·65 obtained for β above

$$\gamma = 1 + \frac{2}{3(1{\cdot}65)} = 1{\cdot}404.$$

It seems reasonable to suppose that the more complicated the molecule the greater will be the work expended in producing intra-molecular motions, and the simpler the molecule the less will that quantity be. Chemists have reason to believe that a molecule of mercury contains only one atom. If that be so, no heat is expended in doing intra-molecular work, and $\beta = 1$, which gives for γ the

value 1·66. Kundt and Warburg have found the ratio γ for mercury by determining the velocity of sound in mercury vapour (Art. 261), and obtained the value 1·67.

The same method gives for helium the value 1·63, and for argon 1·65. Boltzmann considers that the molecule of a gas for which $\gamma = 1·66$ behaves in molecular concussions as a rigid sphere.

Where γ has a value about 1·41, as in nitrogen, oxygen, and hydrogen, the molecule behaves as if it consisted of two spheres rigidly joined together.

For many gases generally triatomic, such as carbon dioxide and sulphuretted hydrogen, the value of γ is about 1·3, and as the molecule becomes more complicated the value of γ becomes more nearly equal to 1.

237. RADIATION.—In the phenomenon of radiation, energy is transferred from one body to another by movements in the ether which are of the nature of undulations.

Thus heat, while on its journey from one place to another by radiation, has ceased to be heat as we ordinarily use that term. It has been transformed into radiant energy.

The regularly recurring series of states in the ether which are termed undulations have their origin in the vibratory movements of molecules, atoms, and electrons.

The visible spectrum of a rarefied gas consists of bright lines only. The rate of vibration corresponding to these lines is so great that many thousands of them take place in the interval between two molecular collisions. Hence it is supposed that these vibrations are independent of molecular motion, and are due to the motions of the atoms and electrons themselves. Each element gives a different set of lines, each line corresponding to a definite rate of vibration.

The spectra of compressed gases, of liquids, and of solids are more complicated. The molecules being closer together, their free path is shorter, and the disturbances introduced by a collision have not time to die away before those produced by the next collision come into play. The effects of the collisions remain as a permanent feature of the spectrum. Those effects are to generate vibrations of other periods than those due to the undisturbed motions of the electrons. The spectrum of a compressed gas is therefore less discontinuous than that of a rarefied gas, and the spectra of liquids and solids are continuous.

The fact that as the temperature of a solid is raised its spectrum is extended in the direction of the rays of shorter wave length shows

that the greater energy of the collisions has the effect of generating vibrations of shorter periods.

238. EXAMPLE.

The specific heat of hydrogen is 3·4. On the supposition that this does not vary with the temperature, and that at -273° C. the molecules would be wholly deprived of motion, find their rate of motion at 0° C.

If one gramme of hydrogen be warmed from -273° C. to 0° C. it would on this supposition absorb $273 \times 3{\cdot}4 = 928{\cdot}2$ calories $= 38613 \times 10^6$ ergs.

According to the dynamical theory of heat it is immaterial whether we consider this energy to have been expended in producing molar or molecular motion. If it produced molar motion we should have for the kinetic energy of the mass

$$\tfrac{1}{2}mv^2 = 38613 \times 10^6,$$
$$\text{but } m = 1.$$
$$\therefore v = 10^3 \times \sqrt{77226}$$
$$= 278000 \text{ cm. per second.}$$

The supposition that the specific heat remains invariable is of course inadmissible, but the result is of the same order of magnitude as that obtained by the ordinary method (Art. 232).

EXERCISES

1. A cubic foot of air at 0° C. under a pressure of 2117 lb. per square foot contains ·0807 lb. Find the velocity of mean square of the particles.
2. What is the supposed cause of the increase in the temperature of a gas when its volume is diminished by pressure?
3. Find the increase of velocity of the molecules of hydrogen (in feet per second) when its temperature is raised 1° C.

CHAPTER XXI

INTERNAL AND EXTERNAL WORK

239. EXTERNAL WORK WHEN A GAS EXPANDS.—When heat is evolved or absorbed by a body, more than one change often takes place. Thus, when a mass of iron gives out heat, its temperature falls and its volume decreases; when ice at 0° C. absorbs heat, its physical condition changes and its volume diminishes. Nothing has been hitherto said here as to how much heat would be required to effect each of these changes separately; but they may be separately considered, as each related to a definite quantity of energy which has passed into or out of the substance during the change.

That heat is absorbed when a mass of gas is allowed to expand under pressure is proved by the following experiment: Let a cylinder of compressed air be taken at the same temperature as the atmosphere, and the tap turned so that a jet of air rushes out against the bulb of a thermometer, the mercury will fall, showing that the escaping air has become chilled in the process of expansion.

What has become of the heat that has thus disappeared? It has been converted into mechanical energy. At the mouth of the tap there was a pressure of nearly 15 lb. on the square inch. The issuing air in occupying a greater volume did work against this pressure, and the heat-equivalent of the work done was abstracted from the air itself, the thermometer, and neighbouring bodies. When an increase of volume takes place under pressure, work is done against that pressure, and if mechanical energy be not supplied to effect the work, heat disappears. Thus, if we heat a gas under atmospheric pressure so that it increases in volume by 1 c. ft., we must do upon it about 15 foot-pounds of work to effect that change of volume, quite independently of any other change, such as change of temperature. Such work is called *external work*, because it is done against the action of *external forces*, i.e. forces outside the body we are considering. Since gases expand largely when heated, the external work done is great, and forms a large part of the whole energy expended in heating them.

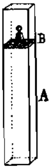

Fig. 165

Suppose 1 grm. of air to be confined within a vertical tube A (fig. 165) whose section is 1 sq. cm., and which is closed at the top by a tightly fitting piston B. Then since the standard pressure of the atmosphere is 1033·3 grm. weight per square centimetre, we can imagine the atmosphere to be replaced by a weight of 1033·3 grm. upon the piston. The height of the enclosed column of air whose mass is 1 grm. is about 773·3 cm. at 0° C.

If the air be heated to 1° C., the piston will ascend through 773·3/273 cm. and the work done against the pressure on the piston = W = 773·3/273 × 1033·3 gramme-centimetres = 2926·9 × 981 ergs = 2871300 ergs. This is the amount of external work done when 1 grm. of air is heated through 1° C. under standard atmospheric pressure.

In general symbols, writing V for the volume occupied by unit mass, P for the pressure, and θ for the absolute temperature, then

the external work done is

$$W = \frac{PV}{\theta} = R.$$

The general form of the expression shows that it holds for any gas.

Since we are dealing with unit mass of the gas, V is the reciprocal of the absolute density ρ. Hence

$$W = \frac{PV}{\theta} = \frac{P}{\theta\rho} = R.$$

The quantity $PV \div \theta$ denoted by the symbol R is by the laws of Boyle and Charles constant for the same given mass of gas, whence it follows that the external work done by any given mass of any gas when its temperature is raised one degree is the same, whatever may be its volume, temperature, and pressure. If the mass of gas be that of 1 gramme-molecule, then the value of R is approximately 82900000 for all gases that obey Boyle's law (Art. 100).

We may also consider the total energy required to heat the gas and to effect the expansion under pressure. Suppose unit mass of gas to be heated and not allowed to expand, then the energy required to raise the temperature of the gas by an amount $d\theta$ is $C_v d\theta$, where C_v is the specific heat of the gas at constant volume expressed in heat units (Art. 77). If at the same time the gas expand under a constant pressure P by an amount dV (the quantity $\frac{V}{\theta}$ above), then work is done to the amount PdV (Art. 207). If PdV be also expressed in heat units, then the total heat dH required to effect the whole change is

$$dH = C_v d\theta + PdV.$$

It is assumed here that no internal work has been done (Art. 241).

240. EXTERNAL LATENT HEAT.—When a liquid is converted into a gas there is a great increase of volume. Work is therefore done in overcoming atmospheric pressure, and the energy required to effect this is called the **external latent heat**, or latent heat of dilatation. The difference between this and the total energy absorbed is the internal latent heat.

Its value for any particular substance may be thus found. When a cubic centimetre of water is boiled away into steam at 100° the steam occupies about 1670 c.cm. During the change the

atmospheric pressure, which is 1033·3 grm. per square centimetre, has been forced back through 1669 cm. The work done is therefore approximately $1670 \times 1033{\cdot}3$ *gramme-centimetres*, which is equivalent in heat units to $\frac{1670 \times 1033{\cdot}3}{42600} = 40{\cdot}9$ calories.

Thus, when unit mass of water is evaporated at 100° C., about 41 units of heat are absorbed in doing external work, and $540 - 41 = 499$ in doing internal work.

241. JOULE'S EXPERIMENTS ON INTERNAL WORK.—Joule investigated the question whether any expenditure of energy was necessary to cause a gas to expand when there was no external pressure upon it, and when, therefore, no external work was done. The gas is certainly in a different condition after the process. Is any work done solely in producing this change of condition? Mayer, on the strength of an experiment made in 1807 by Gay-Lussac, assumed a negative answer to this question; Joule proved that this supposition was approximately correct by the following experiments in which compressed air expanded into a vacuum, and was not found to be cooled as is the case when it expands into the atmosphere (Art. 239).

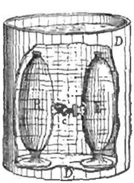

Fig. 166

Two strong copper vessels R and E (fig. 166), each having a capacity of about 2000 c.cm., were connected by a short tube in which was a stopcock *c*. One vessel, E, was exhausted of air; the other, R, was filled with compressed air at a pressure of 22 atmospheres.

The apparatus was then immersed in about 7000 grm. of water contained in a double-walled iron vessel D. On the stopcock being turned the air rushed from R into E until the pressure in each was the same. The temperature of the water in D was read, before and after the expansion of the air, on a delicate thermometer reading to $\frac{1}{200}$ degree Centigrade. This thermometer showed no change of temperature, and Joule therefore concluded that "no change of temperature occurs when air expands in such a way as to do no external work".

Joule varied the experiment by placing each of the air chambers R and E in a separate vessel containing water (fig. 167). In that case he found a fall of temperature in the vessel containing R, where

the air underwent expansion, and an almost equal rise of temperature in the vessel containing E, in which the air underwent compression.

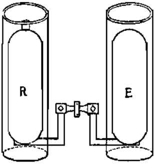

Fig. 167

The setting of the mass of air in motion demanded an expenditure of energy which was obtained at the expense of the sensible heat of R; the destruction of this mechanical motion in E caused there a corresponding evolution of sensible heat.

242. EXPERIMENTS OF THOMSON AND JOULE.—On comparing the heat capacities of the air and water in the above experiment, it is found that it would require a change of temperature in the enclosed air amounting to 2° C. in order to produce a change capable of detection by the thermometer outside.

Lord Kelvin, then Sir William Thomson, was led by theory to believe that the assumption of Mayer, apparently justified by Joule's result above, was not rigorously correct, but that a more sensitive apparatus would show that some change of internal energy does take place when the density of a gas changes, or as it may be expressed, "the heat evolved from air when compressed at constant temperature is not equivalent to the work spent in effecting the compression".

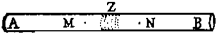

Fig. 168

A very sensitive method was therefore devised on the following principle:—

Let AB (fig. 168) represent a long tube having at one point Z a porous plug containing a large number of small orifices. Air or one of the more perfect gases was forced through the tube in a slow continuous uniform stream. The pressure of the gas at a point M before entering the plug was sometimes several atmospheres, while at N the pressure was simply that of the atmosphere, so that between these points there was a great expansion of the gas. Elementary experiments with a single orifice at Z showed a great cooling, due to the conversion of sensible heat into the mechanical energy of motion of the rapidly issuing air. But at a distance of a few inches from the orifice the energy of motion was all reconverted into heat. Hence with the gas in this condition no external work had been done, and the temperature at N should be the same as at M, provided that no communication of heat took place between the appa-

ratus and external sources, and provided that Mayer's hypotheses were correct, and also that the gas was one which rigorously obeyed Boyle's law. For the internal work done on unit mass of the gas was equal to PV, the product of its original pressure and volume, and that done by the gas on the atmosphere was equal to P^1V^1, the product of the final pressure and volume. If $PV = P^1V^1$ then it would follow that any difference of temperature between M and N was due solely to a change in the internal energy of the gas. But it is shown in Art. 120 that when a gas expands PV is not equal to P^1V^1 (i.e. no gas rigorously obeys Boyle's law), and this *inequality* between the work done on and by the gas would lead to a change in its temperature quite *independently* of any change due to the action of the intermolecular forces. Hence the difference of temperature actually observed is *the algebraic sum of the separate* effects of two causes. The heating or cooling effect due to the departure from Boyle's law is, however, calculable from the data of Amagat's experiments and the specific heat of the gas. Thus *the two effects were separated*, and the change of temperature due to change in the internal energy of the gas determined. The *deviation from Boyle's law gives* a small cooling effect for gas other than hydrogen, and a very small heating effect for hydrogen

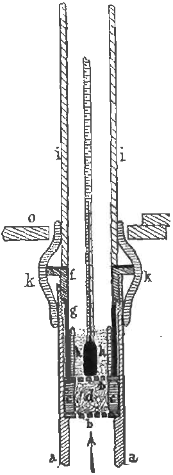

Fig. 169

Various forms of orifice were tried. With a simple aperture the gaseous currents were of so confused a character that very different readings of the thermometer were obtained in slightly different positions, and it was necessary that the mechanical energy of the expanding air should be completely reconverted into heat before it reached the thermometer. The form of porous plug finally adopted is shown in fig. 169.

It consisted of a short piece of indiarubber tube *cc*, closed at each end by a perforated metal disk *bb*, and having the space *d*

inside stuffed with silk. This plug rested on a shoulder of the copper tube *aa*, and was kept in its place by a screw *f* pressing on a tube *g*. The thermometer bulb was surrounded by a tube of cork *hh* filled lightly with cotton wool. By means of an indiarubber tube *kk* the copper tube was connected with a glass tube *ii* to allow the thermometer to be seen.

The gas to be experimented on was forced, by means of a pump D worked by a steam engine, through a tube *bb* (fig. 170), then

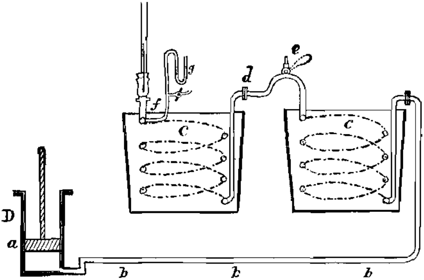

Fig. 170

through two long spirals *cc* immersed in large vessels of water, whence it passed through the porous plug *f*.

In the spirals the gas took up a definite temperature indicated by thermometers in the water. Special care was taken to ensure that the gas was really at the temperature of the water, and to prevent irregularities in the stream of air due to the pulsations of the pump.

The gas was thus made to pass from a high pressure to that of the atmosphere without acquiring sensible mechanical energy, and therefore without doing sensible external work. The work done by the pump on the gas was equal to the work done by the gas in forcing back the atmosphere; no external work was done by the gas at the expense of its own heat.

The results of the experiments were that with no gas was the temperature at N (fig. 168) the same as at M; with air, oxygen,

nitrogen, and carbonic anhydride, there was a fall of temperature at N; with hydrogen, there was a rise of temperature. This proved that the thermal changes taking place when gas is compressed or expanded at constant temperature are not exactly equivalent to the work done on or by the gas. The equivalence would be perfect only with a perfect gas, in which there is no attractive nor repulsive force between the molecules. With actual gases, work is done by or against molecular forces; in air, oxygen, nitrogen, and carbonic anhydride, which deviate from Boyle's law in one direction (see Art. 120), the molecular attractions and the deviations from Boyle's law act in the same direction; both tend to produce cooling. In the case of hydrogen the two causes act in opposite directions.

The cooling effect is due to the fact that work has to be done in *separating the molecules in opposition to their mutual attractions, and the experiments therefore show that there is an attraction between the molecules of a gas at short distances.*

The amount of difference of temperature between M and N was proportional to the difference of pressure, being about ·26° C. per atmosphere for air, and 1·25° C. for carbonic acid. The cooling effect was much greater for gases readily capable of liquefaction. The amount of cooling after passing through the plug—i.e. the amount of internal work—was found to be much less at high than at low temperatures; thus, for carbonic acid at 20° it was 1·15°, while at 91° it was only ·7°.

At the temperature 20° C., the ratio $\frac{\text{internal work}}{\text{external work}}$ is for carbonic acid $\frac{1}{125}$, for air $\frac{1}{500}$, and for hydrogen only $\frac{1}{1250}$.

243. EXAMPLES.

1. Water is forced through a porous plug under a pressure of 50 kg. per square centimetre above the atmospheric, and emerges with negligible velocity at the pressure of the atmosphere. *Assuming that there is no loss or gain of heat from* external sources, find the rise of temperature of the water if 427 kg.-m. are equivalent to 1 kg.-calorie.

Suppose 1 grm. of water to be contained in a tube whose area is 1 sq. cm., then the work done in driving the water through the plug is 50000 grm.-cm.

But 427 kg.-m. = 1 kg.-calorie

∴ 427 × 1000 × 100 grm.-cm. = 1000 grm.-calories

∴ 42700 grm.-cm. = 1 grm.-calorie.

∴ Rise in temperature = 50000 ÷ 42700

= 1·17° C.

2. *Show how to calculate the expansion required to cool a mass of air* 1° C. *if* no heat is supplied.

Under these circumstances the work done by the gas is equivalent to the heat that it has given out. If the working difference of pressure (supposed constant) that produces the expansion be P and the increase of volume be dV, then the work done $= P\,dV$ in work units or $P\,dV \div J$ in heat units. This is equivalent to the quantity of heat that has disappeared, which is C_p, the specific heat of the gas.

$$\therefore dV = \frac{C_p J}{P}.$$

QUESTIONS AND EXERCISES

1. Why is it that with a gas under atmospheric pressure the quantity of heat necessary to produce a given change of temperature varies with the height of the barometer?
2. Describe the changes which take place when heat is applied to 1 lb. of ice at 0° C. until it is converted into vapour. Account for the difference in the quantity of heat required according as the ice is in an open or in a closed vessel.
3. Find the external work done in raising 10 grm. of air from 0° to 15° at constant pressure when the barometer stands at 710 mm.
4. A cubic foot of water is heated from 0° to 100° under standard atmospheric pressure. Find the external work done, the volume of the water having increased by 4 per cent during the operation.

CHAPTER XXII

ISOTHERMAL CURVES—CONTINUITY OF STATE

244. ISOTHERMAL AND ADIABATIC CHANGES.—The absorption or evolution of heat by bodies is accompanied by changes in one or more of their distinguishing physical properties, viz. volume, pressure, and temperature, and the relations between any pair of these variables may be very conveniently shown by curves. Such diagrams are often used also to indicate a further result of importance, viz. the work done during the process.

We proceed first to deal with gases and vapours. The changes in volume and pressure may take place under either of two conditions, according as the temperature remains constant or is allowed to change during the operations.

Thus, suppose we have a quantity of air contained in a metal cylinder. If this air be slowly compressed its temperature will remain constant unless disturbed by external causes, for any heat that may be developed by compression will become dissipated.

Suppose, however, the air to be contained in a cylinder of wood, and the compression to take place quickly. The heat developed during the compression cannot readily escape, so that at the instant after compression, the temperature and therefore the pressure of the air are considerably higher than would be the case if the operation had taken place slowly in a metallic vessel. When a gas changes in volume and pressure under such conditions that the temperature *remains constant, the change is said to take place* **isothermally**, *and* the curve that represents the relation between pressure and volume is called an **isothermal curve**. When the operation takes place under such conditions that no heat enters or leaves the substance during the process the change is said to take place **adiabatically**, and the curve that represents the relation between pressure and volume is called an **adiabatic curve**.

Adiabatic changes will be considered more fully in Chap. XXIV. We now proceed to indicate the characteristics of isothermal curves.

245. CONSTRUCTION OF AN ISOTHERMAL CURVE.—Suppose 10 *c. ft. of air* at 0° C. to be enclosed under a pressure of one atmosphere in a long cylinder of unit sectional area in which works an air-tight piston. By applying pressure to the piston it can be gradually forced down the cylinder, and if the temperature remain constant throughout, Boyle's law is applicable, so that the product PV is constant, and we obtain the following values:—

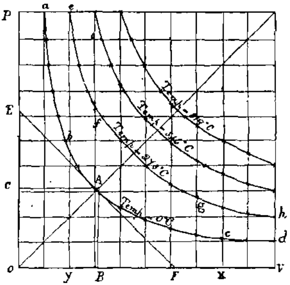

Fig. 171

Volume:—	10	9	8	7	6	5	4	3	2	1
Pressure in Atmospheres:—	1	1·11	1·25	1·43	1·66	2	2·5	3·33	5	10

Now draw two lines OV and OP at right angles to each other (fig. 171). The point O is called the origin, OP is the axis of pressure, and OV the axis of volume. Along OV mark off successive lengths in the ratio of the numbers indicating the volumes above, and at the points thus obtained set up successive perpendiculars whose lengths represent the corresponding pressure. A series of points is thus determined through which a continuous line is drawn, and we obtain the curve *abcd*, which represents the relation between the pressure and volume of the air at the particular temperature chosen.

Suppose that the air be now allowed to expand to its original volume and the temperature raised to 273° C., the pressure will then be two atmospheres and the product PV = 20. If the whole series of operations be repeated at 273° C. we obtain the following series of values:—

Volume:—	10	9	8	7	6	5	4	3	2
Pressure in Atmospheres:—	2	2·22	2·5	2·86	3·33	4	5	6·66	10

and by proceeding as before we obtain the curve *efgh*.

In fig. 171 the curves are also shown for temperatures 546° C and 819° C. These curves are isothermal curves.

246. CHARACTERISTICS OF ISOTHERMALS FOR A PERFECT GAS.—Since an isothermal curve is constructed on the supposition that the product PV is a constant quantity, the area of the rectangle OBAC is constant, whatever may be the position of the point A on the curve. The curve which possesses this property is called a **rectangular hyperbola**, and the axes OV and OP are called the **asymptotes**. As the curve is extended each branch continually approaches one of the asymptotes, but never reaches it. This means that as the pressure increases the volume of the gas continually diminishes, but can never become zero; as the pressure decreases the volume may increase to an indefinite extent.

If a line OA be drawn bisecting the angle POV, then AB × OB = half the square on OA, i.e. for any point on the curve the product PV is proportional to OA^2, but PV is proportional to the absolute temperature (Art. 54); therefore $(OA)^2$ is proportional to the absolute temperature of the gas.

If a tangent be drawn to the curve at any point A meeting the axes in E and F then OC = CE and OB = BF. The length EC represents the elasticity of the gas and OC its pressure; these two quantities are equal.

The isothermals of a gas at higher temperatures lie farther away from the axes than those of lower temperatures. A little consideration will show that the curves never cut each other.

247. ISOTHERMALS FOR THE "PERMANENT" GASES.—A perfect gas is one in which the internal work (Chap. XXI) is *nil* and which therefore rigorously obeys Boyle's law. As no such gas exists, the foregoing curves do not accurately represent the behaviour of any actual gas. They present, however, a type towards which the isothermals of actual gases approximate. The "permanent" gases—air, oxygen, nitrogen, and hydrogen — approximate so closely to this type that refined experiments are necessary to indicate any departure at ordinary temperatures. The nature of that departure is indicated in fig. 172, where the isothermal of a perfect gas is given for comparison. It was shown in Art. 120 that as the pressure is increased hydrogen occupies a greater and other gases a less volume than that assigned by the law. For the sake of clearness in the figure the amount of deviation from the theoretical curve is much exaggerated.

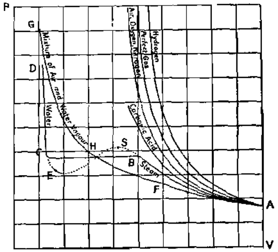

Fig. 172

248. ISOTHERMAL OF A VAPOUR.—Suppose steam to be operated upon, the vapour being in its initial condition at 100° C. and at a very small pressure. Under these conditions the vapour very nearly obeys Boyle's law. As the pressure increases and the volume diminishes the vapour gradually approaches the condition of saturation; the volume decreases at a greater rate than Boyle's law indicates, and the isothermal AB in fig. 172 falls below that of the

more perfect gases. When the condition is reached which is represented by the point B on the diagram, the steam being saturated, the slightest increase of pressure causes some of it to be condensed into water. If then the piston descend slowly the pressure continues constant at the maximum value for the assigned temperature; and the volume steadily diminishes until the whole has become water. This part of the isothermal is thus a horizontal line BC. If the pressure be still further increased the change of volume of the liquid is very small for a great increase of pressure, and the isothermal becomes an almost vertical line CD.

It is possible to prolong the line AB to the point S, for by great care under certain conditions a saturated vapour may be subjected to a small increase of pressure without condensation taking place.

And so in the converse operation water may be prevented from evaporating when the pressure is lowered to the value corresponding to the point E on the diagram. In both these cases, however, the slightest shake produces the change in a violent manner. As these two small portions CE and BS are practically obtainable, the theoretical curve between B and C is of the form BSEC which is not discontinuous.

A set of isothermal lines for water-steam would present the same characteristics as those drawn for carbonic acid in fig. 173, the lowest isothermal of fig. 173 corresponding approximately to the water-steam isothermal of 0° C., the next to that of 100° C., and the third to that of 380° C., just above the critical temperature of steam (Art. 251).

249. MIXTURE OF GAS AND VAPOUR.—If a mixture of air and water vapour be compressed isothermally the diagram takes the form shown in AFG (fig. 172), which is a correct isothermal for such a mixture at 60° C. The original volume at A is 10 and pressure 16·6, of which 7·68 is due to air and 8·92 to the water vapour, the pressure being measured in centimetres of mercury.

The mixture is compressed until the volume is 6 and the pressure 27·7, which is made up of pressures of 12·8 and 14·9 for air and vapour respectively. Assuming that the mixture obeys Boyle's law, the curve AF is a hyperbola. When, however, the point F is reached the pressure of the water vapour has reached its maximum for the temperature and augments no further. When the mixture is further compressed the diminution of volume is accompanied by an increase of the air pressure but not of the vapour pressure. Thus when the volume is 5 the pressure is 30·3, viz. 15·4 due to the air

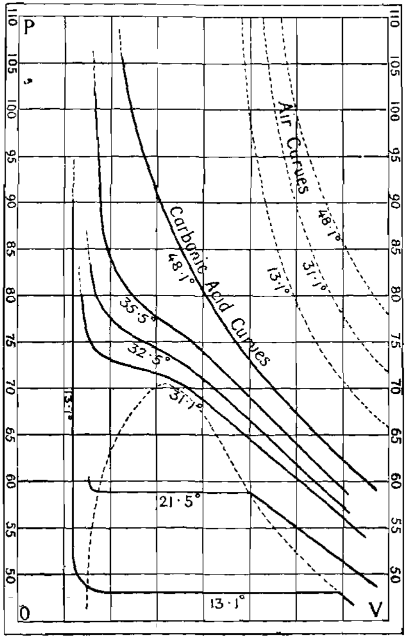

Fig. 173

and 14·9 due to the vapour, and so on. The portion FG is therefore not a hyperbola, and the whole curve AFG is broken into two parts at F.

250. CARBONIC ACID.—The method and general results of

the experiments of Andrews on carbonic acid are given in Art. 121. We give in fig. 173 the isothermal lines of this substance for several different temperatures, the pressure being in atmospheres and the volume in arbitrary units

Isothermal at 13·1° C.—Starting with a quantity of gas at this temperature the pressure was gradually increased up to 47 atmospheres, the substance remaining so far in the gaseous state, and the curve (not shown in this figure) being of the form given in fig. 172. At a pressure of about 47 atmospheres, when the volume was about 7 units, condensation began, in exactly the same way as with steam, the liqnid and gas being in contact with each other, with a well-defined snrface of separation. The pressure remained almost constant as liqnefaction proceeded, as is indicated by the horizontal line. The whole when liquefied occupied about 1·2 volume. The contraction of volume in liquefaction was much less than in the case of water and steam.

Isothermal at 21·5° C.—At this temperatnre the substance remained wholly in the gaseous state until the pressure reached about 60 atmospheres and the volume about 5 units. Condensation then took place as before at constant pressure, and the isothermal becomes horizontal. The whole when liquefied occupied about 1·5 vol.

Thns it appears that at the higher temperature the gas was much more dense hefore condensation began, while the liquid produced was much less dense than before. The two states were approximating to each other.

At temperatures between 21° and 30° this approximation continues, the horizontal line in the diagram becoming shorter and shorter as the temperature is raised, until at 30·92° the horizontal line vanishes, i.e. there is at that temperature no period during which liquid and vapour can be separately distinguished.

Isothermals at 31·1°, 32·5°, 35·5°.—At these temperatures as the volume diminishes under the increasing pressure there is no part of the line perfectly horizontal, because the pressure never remains quite constant as the volume diminishes. The substance is never in two distinct conditions in different parts, but remains in a homogeneous state throughout the tube.

At 48·1° and above, the isothermals exhibit no divergence in general character from the ordinary type for a gas.

251. CRITICAL TEMPERATURE.—The temperature 30·92° is the critical temperature for carbonic acid. At that temperature

and at about 74 atmospheres pressure, the substance is in the critical condition (Art. 121). A glance at the diagram will show that when in the critical condition the substance is less than half the density of the ordinary liquid.

Below 30·92° C. it is possible for liquid and gaseous carbonic acid *to exist together in the same tube*; above that temperature such coexistence is impossible, whatever pressure be applied.

252. WORK DONE DURING ISOTHERMAL CHANGE OF VOLUME.—It is an important problem to ascertain how much work is done on a gas when it is compressed isothermally. Referring back to Art. 245 and fig. 171 let us consider the work done in compressing the gas from 8 c. ft. to 2 c. ft. at 0°. The working force is always equal to the pressure of the gas, and the distance worked through by the force is the length moved through by the piston, which *is proportional to the diminution of the volume*. The area marked out cannot be a rectilinear figure because the pressure of the gas is continuously increasing throughout the whole operation. The area *xcby* (fig. 171) represents the work done in this instance, and the problem is to determine that area.

As a rough approximation we may take the mean of the ordinates which are given in Art. 245 to represent the mean pressure, and multiply by the distance $xy (= 6)$. This gives for the area $2{\cdot}45 \times 6 = 14{\cdot}7$.

The rule given in Art. 208 gives a much better result. According to that the area is

$$\tfrac{1}{3}\{1{\cdot}25 + 5 + 8{\cdot}32 + 27{\cdot}04\} = 13{\cdot}87,$$

which is very near the truth.

The above, however, are mere approximations. The correct value when the curve is a hyperbola, i.e. when a gas obeys Boyle's law, is obtained as follows:—

Let the original pressure and volume respectively be P_1 and V_1, then since the temperature remains constant $P_1V_1 =$ a constant; call this constant A.

Now suppose an extremely small decrease of volume dV_1 to take place, then the work done on the gas is $P_1dV_1 = A\frac{dV_1}{V_1}$ where $\frac{dV_1}{V_1}$ is a very small fraction.

If then the process be split up into an extremely large number of such steps, we see that the total work done $= A \times$ (the sum of a large number of small fractions). These small fractions are no two

of the same value, so that their summation is only possible by the calculus. Integrating we have

$$\begin{aligned} W &= A\int_{V_2}^{V_1} \frac{dV}{V} \\ &= A\,(\log_e V_1 - \log_e V_2) \\ &= P_1V_1 \log_e \frac{V_1}{V_2} \text{ or } P_2V_2 \log_e \frac{V_1}{V_2} \\ &= P_1V_1\,(\text{or } P_2V_2) \times 2{\cdot}302585 \times \log_{10} \frac{V_1}{V_2}. \end{aligned}$$

If P = pressure in	and V = volume in	then W = work in
(a) pounds per sq. foot,	(a) cubic feet,	(a) foot-pounds.
(b) grammes per sq. centimetres,	(b) cubic centimetres,	(b) gramme-centimetres.

Applying this to the above example we have—

$$\begin{aligned} W &= 10 \times 2{\cdot}302585 \times \log_{10} \tfrac{8}{2} \\ &= 23{\cdot}02585 \times {\cdot}60206 \\ &= 13{\cdot}864 \text{ in terms of the foot and the atmosphere.} \end{aligned}$$

In foot-pounds W = 13·864 × 2117 = 29350, the standard pressure of the atmosphere being 2117 lb. per square foot. The result of this Article has been anticipated in Art. 216.

253. Suppose this 29350 foot-pounds of work to be spent in warming the mass of air operated upon, its temperature being originally 0° C., and the volume remaining at 8 c. ft.

These 29350 foot-pounds of work = 29350 ÷ 1390 = 21·1 pound-degrees of heat.

Also the mass of air in 1 c. ft. at atmospheric pressure and at 0° C. = ·0807 lb., therefore the mass of air in 8 c. ft. at 1·25 atmos. pressure is ·0807 × 8 × 1·25 = *·807 lb. The specific heat of air at constant volume is ·168. Thus the heat* absorbed by the air while its temperature was rising 1° C. is ·807 × ·168 = ·1356 pound-degrees.

Therefore the temperature to which the air would be raised is $\frac{21{\cdot}1}{{\cdot}1356} = 156°$ C. nearly.

254. Isothermal lines may also be drawn showing graphically the *changes of pressure and volume when a substance changes from the* solid to the liquid state, but the changes of volume that ensue with change of pressure are so small that such diagrams cannot be drawn to scale.

Ice-water.—This substance occupies less volume as a liquid than as a solid, and cannot be got as a solid above 0° C. The line ABCD (fig. 174) represents the isothermal for the temperature corresponding

to the triple point (·0074° C., Art. 106). In the condition represented by the point A the ice is under a small pressure. As the pressure is increased to one atmosphere (point B) there is a diminution of volume *of the ice. Further, under* this pressure the ice liquefies and there is a further diminution of volume, the line BC being traced out. At C all the ice is melted. Further, great increase of pressure produces a small reduction in volume, and the line CD is traced out.

For a temperature $-x°$ C. the isothermal would take the position of the dotted line.

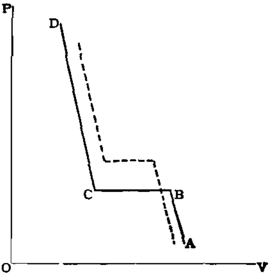

Fig. 174

255. THE EQUATION OF VAN DER WAALS.—The equation

$$PV = R\theta \text{ ....(1)}$$

not being an adequate expression of the gaseous laws, a step towards a more complete expression has been made by van der Waals, who writes the equation thus—

$$\left(P + \frac{a}{V^2}\right)\left(V - b\right) = R\theta \text{ ....(2)}$$

the new terms being introduced to satisfy considerations the outline of which we endeavour to give.

With reference to the factor $(V - b)$ consider a mass of gas confined in a tube and subjected to gradually increasing pressure. As compression proceeds, the molecules are forced closer together, the same number occupying a smaller chamber. Now, in equation (1) V expresses the volume of this chamber. But the molecules themselves must occupy some space x if they were packed together at rest like billiard balls in a box; and although under ordinary conditions this space x is very small compared with V, the volume of the chamber they occupy, yet rigorously it should not be neglected. The volume we are dealing with is not V but some smaller volume $V - b$. The

quantity b depends on, but is not equal to x above, because the molecules of the gas are not at rest like billiard balls in a box, and the effect of their motion is to increase this "volume correction" from x to a larger quantity b, which van der Waals calculates to be equal *to four times the actual volume of the particles.*

With reference to the factor $\left(P + \frac{a}{V^2}\right)$ consider the effect of the molecular forces existing between the molecules themselves. The porous-plug experiments (Art. 242) prove that the molecules of a *gas attract each other with a force which increases the nearer they* are together. The result of this inter-molecular attraction is to produce a general tendency of the gas to shrink into a smaller volume, i.e. to diminish the resistance which the gas would offer to compression. This produces the same result as an increase in the external pressure P. *Thus the force producing compression is* $P + x'$, the sum of the external pressure P and the force x' due to molecular attraction. This molecular force being proportional to the prodnct of two attracting masses, is proportional to the square of the density of the substance. Hence the quantity x' varies inversely as the square of the volume V, *and is therefore written* $a \div V^2$. *Thus* we have equation (2) above. The results, given in Art. 120, are by this equation easily capable of explanation. So long as P was less than the pressure of 59 metres of mercury the effect of the volume correction b was for most gases smaller than that of the correction for molecular attraction $\frac{a}{V^2}$, but when P was greater than that pressure, the latter correction was greater than the former. The reverse holds good for hydrogen, in which gas the force of molecular attraction appears to be very small. The results of Amagat's experiments are much more in accordance with the equation of van der Waals than with that of Boyle.

But the equation of van der Waals goes further than to furnish some explanation of the relations between the pressure, volume, and temperature of a mass of gas. It constitutes also an important step towards the formulation of the connection between the gaseous and liquid states. *When near the critical state the molecular conditions* of a substance are found to be much the same whether it is liquid or gaseous. Whence it appears that molecular energy is a function rather of temperature than of physical state, and that the same general law holds good for a simple homogeneous substance through both conditions—*liquid and gaseous.*

The constants a, b, and R *of equation* 2 *above are different* for each gas. The value of a is found from the results of experiments in which P and θ vary while V remains constant; and that of b from the change of V with P while θ is constant. Examining the results of Andrews, Regnault, and Amagat, van der Waals found the following values for carbon dioxide:—$a = \cdot 00874$; $b = \cdot 0023$; $R = 1 \cdot 00646 \div 273$.

Using these values in his equation he obtained a set of curves for different temperatures on the hypothesis that equation (2) holds good whether the substance is gaseous or liquid. These curves are shown in fig. 175, which should be compared with the curves shown in fig. 173, which were obtained experimentally by Andrews.

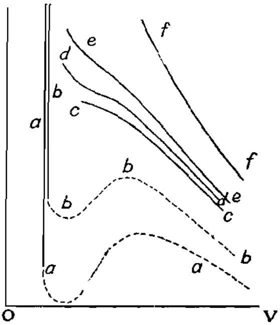

Fig. 175

It is seen that the two sets of curves are for the most part identical. When the value of θ is below the *critical* value, the theoretical curve is of the form shown in the two lower isothermals of fig. 175; when θ is *above* that value, the isothermal takes successively the forms shown in the four upper curves. The difference between the lower curves in the two figures lies in the central part, which represents the behaviour of the substance when it is not homogeneous but is partly liquid and partly gaseous. It had already been suggested by Professor James Thomson, from consideration of the facts mentioned in Arts. 60 and 110, that the correct form of the curves is that shown in fig. 175.

Critical Constants.—By multiplying each member of equation (2) above by $\frac{V^2}{P}$ and rearranging the terms, the equation of van der Waals may be written in the form

$$V^3 - V^2\left(b + \frac{R\theta}{P}\right) + \frac{aV}{P} - \frac{ab}{P} = 0 \qquad \text{..........(3)}$$

a cubic equation yielding three values of V for every given value of P and θ. It follows from the properties of cubic equations that of the three roots of the equation either one must be real and two imaginary or all three must be real. Only real roots have any physical meaning. Thus when there are three different real values of V corresponding to any given pressure P on the same isothermal, as is indicated for the curve *aaa* in fig. 175, the meaning is that the substance can exist in three conditions at this pressure, viz. (1) all liquid, (2) partly liquid and partly gaseous, and (3) all gaseous. As isothermals are taken at successively higher temperatures, these three values of V approach each other, and when they become identical the substance is in its critical state. The values of the volume, temperature, and pressure when the substance is in this state are called the *critical volume* (V_c), *critical temperature* (θ_c), and *critical pressure* (P_c). And then

$$(V - V_c)^3 = 0$$
$$\therefore V^3 - V^2(3V_c) + 3V(V_c)^2 - V_c^3 = 0 \quad \text{.........(4)}$$

Comparing equation 4 with equation 3 we have—

$$3V_c = b + \frac{R\theta_c}{P_c} \quad \text{........................(5)}$$
$$3V_c^2 = \frac{a}{P_c} \quad \text{..............................(6)}$$
$$V_c^3 = \frac{ab}{P_c} \quad \text{..............................(7)}$$

From equations 5, 6, and 7 we obtain—

$$P_c = \frac{a}{27b^2} \quad \text{..............................(8)}$$
$$V_c = 3b \quad \text{..............................(9)}$$
$$\theta_c = \frac{8a}{27Rb} \quad \text{........................(10)}$$

Thus we have the critical constants in terms of a, b, and R. From the values of a, b, and R above, we obtain for carbon dioxide P_c = 61 atmospheres and θ_c = 30·5° C., which agree well with Andrew's values.

Corresponding States.—Two different substances are in *corresponding states* when the ratios between the actual volume, pressure, and temperature and the critical volume, pressure, and temperature respectively are the same for the two substances. Suppose the

actual volume, pressure, and temperature of a substance to be P, V, and θ, then we may write—

$$P = \lambda P_c = \frac{\lambda a}{27b^2}$$
$$V = \mu V_c = 3b\mu$$
$$\theta = \nu\theta_c = \frac{8a\nu}{27Rb}.$$

Substituting these values in equation 2, we have—

$$\left(\lambda P_c + \frac{a}{\mu^2 V_c^2}\right)\left(\mu V_c - b\right) = \nu R\theta_c$$

i.e. from 8, 9, 10 above,

$$\left\{\lambda\left(\frac{a}{27b^2}\right) + \frac{a}{9b^2\mu^2}\right\}\left\{3\mu b - b\right\} = \nu R\frac{8a}{27Rb}$$

which if both sides be divided by $\frac{a}{27b}$ becomes

$$\left(\lambda + \frac{3}{\mu^2}\right)\left(3\mu - 1\right) = 8\nu \quad\quad (11)$$

an equation containing only the ratios mentioned above and independent of any constant referring to any particular substance.

The expression $\lambda = \frac{P}{P_c}$ is called the *reduced pressure*,

$\mu = \frac{V}{V_c}$ the *reduced volume*,

and $\nu = \frac{\theta}{\theta_c}$ the *reduced temperature*.

If one plots on a curve the values of λ and μ for a series of definite values of θ, isothermal lines are obtained which are common to all substances. Such isothermals are called **reduced isothermals**. When λ, μ, and ν are each equal to unity, the isothermal obtained passes through the critical point.

When for any two substances λ, μ, and ν have the same value, the two substances are said to be in a **corresponding state** or **co-incident condition.**

Thus the absolute critical temperatures for ether and carbonic acid are 470° and 304°. If we make $\nu = \frac{3}{4}$, then $\frac{3}{4}\left(470°\right)$ and $\frac{3}{4}\left(304°\right)$ are corresponding temperatures for these two substances.

Again, for ether at 0° C. the diminution of specific volume that results when the pressure is increased by 1 atmosphere is ·00011. The critical pressure for ether is about 36 atmospheres. Now taking chloroform, for which the critical pressure is about 55 atmospheres, we find, from the above figures, for the diminution of volume in chloroform corresponding to the increase of 1 atmosphere in pressure at 0° C. the value

$$\cdot 00011 \times \frac{36}{55} = \cdot 000072,$$

and experiment gives ·000076.

Again, take the case of carbonic acid and ether, for which we have

	Carbonic Acid.	Ether.
Critical temperature ...	304 abs.	470 abs.
Critical pressure ...	72 atmos.	36·9 atmos.

Let the actual pressure P of the carbonic acid gas be 1 atmosphere, then λ for carbonic acid $= \frac{P}{P_c} = \frac{1}{72}$; and the actual pressure of ether vapour in the corresponding state, i.e. where λ has the same value, is $\frac{1}{72} \times 36 \cdot 9 = \cdot 51$ *atmosphere. This is known by experi*ment to be the pressure of ether vapour at 290° (absolute). Thus for ether $\nu = \frac{\theta}{\theta_c} = \frac{290}{470} = \cdot 62$, and the corresponding temperature for carbonic acid $= \nu\theta = 304 \times \cdot 62 = 188°$ (absolute). As the pressure is 1 atmosphere, this temperature (−85° C.) should be the boiling-point of carbonic acid. The value obtained by experiment is −80° C.

These examples illustrate the value of the relations established above in enabling the constants of certain classes of substances to be calculated.

There is in many cases considerable lack of exact agreement between experiment and various deductions from van der Waals' equation. This has led to suggested modifications; but their full consequences have not been developed.

QUESTIONS AND EXERCISES

1. Distinguish between a gas and a vapour. Describe the behaviour of a mass of carbonic acid during the following operations:—

(*a*) The temperature being 15° C. the pressure is gradually increased from 1 to 50 atmospheres; (*b*) at this pressure the temperature is gradually raised to 40° C.; (*c*) the pressure is then slowly reduced to atmospheric.

2. Describe and give the results of Andrews' experiments on the isothermals of liquids and vapours.
3. Plot out a curve showing the relation between volume and pressure of 1 grm. of dry air when the pressure changes from 10 mm. to 760 mm. of mercury, the pressure being read every 75 mm.
4. Find the work done on the air in Question 3: first, approximately from the diagram; secondly, accurately from the result of Art. 252.
5. Find the work done in compressing 2 c. ft. of gas isothermally until its volume is 1 c. ft., the initial pressure being 14·7 lb. on the square inch.
6. If the work done on the gas in the previous examples had been expended in warming it instead of in compressing it, find the rise of temperature.
7. Explain the law of corresponding states, and give illustrative cases in which it may be applied to deduce probable values of the thermal constants for a substance when complete experimental data are wanting.
8. Explain how the densities of a liquid and its saturated vapour have been measured up to temperatures approaching the critical temperature, and show how these measurements may be employed to determine the critical volume.

CHAPTER XXIII

SPECIFIC HEATS OF GASES

C_p = specific heat at constant pressure.
C_v = specific heat at constant volume.
R = the value of the constant $\frac{PV}{\theta}$ for unit mass of gas.
γ = the ratio C_p to C_v.
ϵ = elasticity.
ρ = density.

256. RELATIONS BETWEEN THE SPECIFIC HEATS.—It has been shown that when a gas is heated and allowed to expand under pressure, work is done against that pressure. The energy supplied accomplishes two objects, *the heating of the gas and the overcoming of the external pressure.* If, then, gas be heated under such conditions as to do no external work, the heat required to effect a given rise of temperature must be less than if external work is done. There are, therefore, two values for the specific heat of a gas according as it is measured at constant pressure or at constant volume. Their experimental determination has been described in Art. 77. *But the values of both* C_v *and* C_p were known before either of them had been experimentally determined, as the difference between the two quantities and the ratio between them had been found by other methods. The methods are:—

(i) The difference is found by determining the equivalent of the energy expended in external work.

(ii) The ratio γ is found from observations on the heating and cooling effects which are produced by adiabatic compression and *expansion, and from a comparison of the calculated with the* observed velocities of sound.

257. DIFFERENCE OF THE SPECIFIC HEATS.—$C_v = C_p - R$. In Art. 239 it was calculated that the external work done against the atmosphere when 1 grm. of air expanded from 0° to 1° was 2871300 ergs. That, then, is the amount of the difference between the specific heats of air. Now 1 calorie = 42 × 10^6 ergs. Therefore 2871300 ergs = ·0691 calorie. If we take the value of specific heat of air at constant pressure found by Regnault to be ·2375 calorie, then the value of C_v is ·2375 — ·069 = ·1685 calorie, and the ratio

$$\gamma = \frac{C_p}{C_v} = \frac{2375}{1684} = 1 \cdot 409.$$

As shown in Art. 239, for any gas $C_p - C_v = R$, so that a similar calculation may be made for any gas.

258. RATIO OF THE SPECIFIC HEATS.—When a gas is compressed adiabatically (Art. 268) its temperature rises, and when it expands adiabatically its temperature falls, and the change of pressure or elasticity is sensibly proportional to the change of temperature when those changes are small. The ratio between the two elasticities when a gas expands adiabatically and when it expands isothermally is the same as the ratio between the two specific heats of the gas. The temperature and pressure momentarily attained by the gas during an adiabatic expansion cannot be directly measured. Clément and Désormes, therefore, made the experiment in the following manner:—

A quantity of air at a pressure slightly different from (suppose below) that of the atmosphere, was enclosed in a large glass vessel A (fig. 176). The pressure p_1 of the confined air was measured by a manometer NGF.

A tap M was then opened allowing communication with the atmosphere whose pressure was P.

A rapid equalization of pressure took place between the atmosphere and the air in A. The process was assumed to be complete in about half a second, and the tap was then closed.

During this time the air in A had been compressed, and there was not time for the heat developed during the compression to become diffused, so that at the instant of closing the tap the air in A was hotter than that outside. As it gradually cooled its pressure fell, and when its temperature was again that of the atmosphere, the pressure as measured by the manometer was p_2. The ratio between

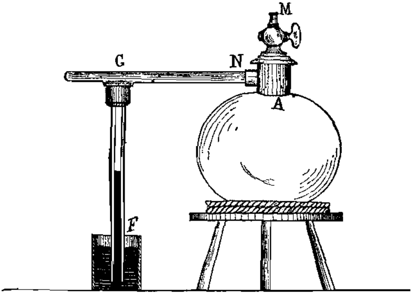

Fig. 176

p_2 and P may be taken as the ratio between the temperatures at the beginning and end of the half-second interval.

Thus, in this adiabatic change the original and final pressures were p_1 and P, and the original and final temperatures were in the ratio of p_2 to P; then by Art. 268, equation B, we have

$$\left(\frac{p_2}{P}\right)^\gamma = \left(\frac{p_1}{P}\right)^{\gamma - 1}$$

$$\therefore \gamma(\log p_2 - \log P) = (\gamma - 1)(\log p_1 - \log P)$$

$$\therefore \gamma = \frac{\log P - \log p_1}{\log p_2 - \log p_1}$$

$$\text{or } \textit{very nearly } \gamma = \frac{P - p_1}{p_2 - p_1}.$$

In one experiment the original pressure p_1 of the confined gas

was ·9953 megadynes; the final pressure p_2 was 1·0088. That of the atmosphere P was 1·0136,

$$\text{then } \gamma = \frac{P - p_1}{p_2 - p_1} = \frac{1{\cdot}0136 - {\cdot}9953}{1{\cdot}0088 - {\cdot}9953} = \frac{{\cdot}0183}{{\cdot}0135} = 1{\cdot}35.$$

Masson and Horn obtained values about 1·4.

This method is liable to error from two sources. The change is not truly adiabatic; every substance conducts heat to some extent, and in half a second the loss by conduction must have been appreciable. And, moreover, a series of oscillations really takes place at M, so that it is very doubtful at the moment when the stopcock is closed what the pressure (assumed = P) really is inside the vessel A.

259. **Röntgen's Method.**—Röntgen modified the method as follows. He employed a glass vessel A (fig. 177) having a capacity of 70 litres (about 2½ c. ft.), and the change of pressure was indicated by means of a special arrangement resembling an aneroid barometer. A circular corrugated plate of German silver *aa* was fastened over an aperture in the side of the glass vessel. To this plate was attached a small rod *b*, which pressed against the back of a mirror *c* that was mounted on a flexible arm *d*, so that when the pressure in A changed, the mirror *c* performed an angular motion round the point *e*, and a spot of light reflected from *c* was thus made to traverse a scale. The aneroid was protected by a vessel B, which communicated by means of a tube *f* with another large glass globe containing air at atmospheric pressure. The quantities observed and the method of experiment were the same as before, except that p_1, the original pressure, was in Röntgen's experiments slightly greater than that of the atmosphere, the result being adiabatic expansion instead of compression.

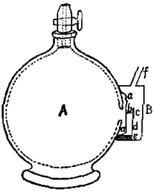

Fig. 177

The value obtained for air was 1·405,
and for carbon dioxide .... 1·305.

260. γ DETERMINED FROM THE VELOCITY OF SOUND.—The following method of finding an expression for the velocity of sound is due to Rankine. Let fig. 178 represent a tube one

square centimetre in sectional area, through which a sound wave is passing with a velocity of x centimetres per second. Then x cubic centimetres of air are disturbed in one second, and if m be the mass in grammes of these x cubic centimetres of air, and V the volume in cubic centimetres of one gramme of air, then

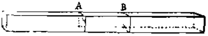

Fig. 178

$$x = mV \text{ or } m = \frac{x}{V} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Imagine two planes A and B moving along the tube in the same direction as the wave and with the same velocity, x centimetres per second. Air particles are continually passing through each of these planes, but the form of the portion of the wave they intercept is invariable.

	In Plane A.	In Plane B.
Let the actual velocity of the air particles be	a	b
Then the velocity of these particles relative to the planes are respectively	$x - a$	$x - b$
And the volume of air passing through the planes per second	$x - a$	$x - b$
And the mass of air passing through the planes per second	$\frac{x - a}{V_1}$	$\frac{x - b}{V_2}$

Where V_1 and V_2 represent the quantity V above, under the conditions present in the respective planes. A little consideration will show as above that

$$m = \frac{x - a}{V_1} = \frac{x - b}{V_2} = \frac{b - a}{V_1 - V_2} \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$\left.\begin{aligned} \therefore a &= x - mV_1 \\ \text{and } b &= x - mV_2 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (3)$$

The same mass m of air passes through plane A and plane B per second, but it has a velocity of a in plane A and of b in plane B. There is therefore a gain of momentum $= m(b - a)$. This is due *to, and equivalent to the difference of the pressures* (P_1 *and* P_2) *in* the planes.

$$\therefore P_1 - P_2 = m(b - a) \quad \ldots\ldots\ldots\ldots \quad (4)$$

but by equation (2) $\quad b - a = m(V_1 - V_2)$

$$\therefore P_1 - P_2 = m^2(V_1 - V_2)$$

$$V\frac{P_1 - P_2}{V_1 - V_2} = Vm^2 = V\left(\frac{x^2}{V^2}\right) = \frac{x^2}{V}$$

but by definition $$\epsilon = V\frac{P_1 - P_2}{V_1 - V_2}$$

$$\therefore \epsilon = \frac{x^2}{V}$$

$$\therefore x^2 = \epsilon V = \frac{\epsilon}{\rho}.$$

Newton found that the velocity of sound in any gas was equal to $\sqrt{\text{elasticity} \div \text{density}}$, but his numerical evaluation did not agree with experiment, because he took the value of ϵ as determined under isothermal conditions.

In the propagation of a sound wave the air is alternately compressed and rarefied many times, usually hundreds of times in a second. These compressions and rarefactions are accompanied by the production and disappearance of heat, but the change takes place so rapidly that the temperatures of the different parts cannot become equalized, and the process is almost a perfect example of that adiabatic compression and expansion attempted to be experimentally obtained in Röntgen's experiments given above. The value of ϵ in the above result is therefore the value of the elasticity determined under adiabatic conditions, not, as Newton supposed, the value of ϵ which is obtained under isothermal conditions, i.e. P. It may be shown that the adiabatic value of ϵ is equal to γP, where P is the pressure of the atmosphere.

$$\text{Therefore } x^2 = \gamma \frac{P}{\rho}, \text{ or } \gamma = x^2 \frac{\rho}{P}.$$

For perfectly dry air at 0° C. and 760 mm. pressure $p = 1{\cdot}0136 \times 10^6$ dynes per sq. cm., and $\rho = {\cdot}001293$ grm. The mean of twelve determinations of x, given in Everett's *Physical Constants*, is 33180 cm. per sec.

$$\therefore \gamma = x^2 \frac{\rho}{P} = (33180)^2 \frac{{\cdot}001293}{1{\cdot}0136 \times 10^6}$$

$$= 1{\cdot}404.$$

The value of γ is usually taken as 1·41.

261. The value of γ being known for air, that of other gases may be found experimentally by the method of Kundt. The apparatus is shown in fig. 179. AA′ is a long glass tube of large bore to contain the gas. One end is closed by a movable stopper B and the other by a fixed stopper B′. Through B′ passes a glass tube D carrying a

lightly fitting stopper C. The tube AA′ contains a small quantity of *some light dry powder such as that of lycopodium. The tube* D *is* rubbed briskly in a longitudinal direction with a damp cloth and a musical note is produced. When the distance between B and C has been suitably adjusted, the lycopodium powder in BC collects into small heaps, and the distance between the heaps is proportional to

Fig. 170

the wave length of the note, and therefore to the velocity of sound in the gas contained in the tube A.

$$\text{Then we have for air } \gamma_1 = \frac{x_1^2\rho_1}{P}$$

$$\text{and for the gas in question } \gamma_2 = \frac{x_2^2\rho_2}{P}$$

$$\therefore \frac{\gamma_2}{\gamma_1} = \frac{x_2^2}{x_1^2}\cdot\frac{\rho_2}{\rho_1};$$

but if l_1 and l_2 are the distances between the heaps of dust,

$$\frac{l_2}{l_1} = \frac{x_2}{x_1} \quad \therefore \frac{\gamma_2}{\gamma_1} = \left(\frac{l_2}{l_1}\right)^2\cdot\frac{\rho_2}{\rho_1},$$

whence the value of γ_2 is known.

262. RANKINE'S CALCULATION OF THE SPECIFIC HEAT OF AIR.—*Rankine calculated as follows the value of the* specific heats of air a year before Regnault determined the value of C_p.

The difference between the specific heats is obtained by the method of Art. 239, and we have thus—

$$R = C_p - C_v = \cdot 0691.$$

The ratio between the specific heats being obtainable as in Art. 260 from the velocity of sound, we have

$$C_p = 1{\cdot}41\ C_v$$

There are thus two independent equations containing the two un-

known quantities. The solution of these equations gives both the quantities sought.

$$\text{Thus} \quad 1{\cdot}41\, C_v - C_v = {\cdot}0691$$
$$\therefore {\cdot}41\, C_v = {\cdot}0691$$
$$\therefore C_v = {\cdot}168$$
$$\text{and } C_p = {\cdot}237.$$

It must be observed that in the calculation of the value of $C_p - C_v$ (Art. 257) on which this calculation is founded, the value of J is involved.

263. CALCULATION OF JOULE'S EQUIVALENT.—When Regnault had determined experimentally the value of C_p, it became possible by taking the value of γ either from Röntgen's experiments or from the method of Art. 260 to calculate J.

If γ be taken as 1·41, C_p being given by Regnault as ·237, we have

$$C_v = \frac{{\cdot}237}{1{\cdot}41} = {\cdot}168.$$

Thus the heat-equivalent of the external work done when 1 grm. of air is raised in temperature from 0° C. to 1° C. under atmospheric pressure is ·237 − ·168 = ·069 calorie. But this work has been shown to be 2871300 ergs (Art. 239), therefore one calorie $= \frac{2871300}{{\cdot}069}$ $= 41{\cdot}55 \times 10^6$ ergs.

Mayer made the earliest calculation of the value of the mechanical equivalent of heat. Taking the data available in his day for the calculation of Arts. 239 and 257, Mayer obtained the value $36{\cdot}5 \times 10^6$ ergs.

264. EXAMPLE.

The specific gravity of a certain gas under a pressure of 75 cm. of mercury at 0° C. is one-thousandth of that of water. What is the velocity of sound in it at that temperature?

$$\text{In the expression } x^2 = \gamma \frac{P}{\rho}$$
$$\gamma = 1{\cdot}4,\ \rho = {\cdot}001 \text{ grm. per c.cm., and}$$
$$P = 75 \times 13{\cdot}6 \times 981 \text{ dynes per sq. cm.}$$
$$\therefore x = \sqrt{\frac{1{\cdot}4 \times 75 \times 13{\cdot}6 \times 981}{{\cdot}001}}$$
$$= 37430 \text{ cm. per second.}$$

QUESTIONS AND EXERCISES

1. Show how to calculate the mechanical equivalent of heat from a knowledge of the specific heats of air at constant pressure and volume respectively, explaining carefully any assumption made in the process.
2. Determine the value of the mechanical equivalent from the following data:— Specific heat of air at constant pressure = 0·2374; velocity of sound in air at 0° C. = 33300 (cm. sec.); mass of 1 c.cm. of dry air at 0° C., and 760 mm. pressure = ·001293 grm.
3. Calculate the value of the specific heat of air at constant volume from the following data: Sp. heat at const. pres. = ·2375; J = 1390 foot-pounds: pressure of the atmosphere 14·7 lb. on the square inch: coefficient of expansion of air $\frac{1}{273}$; mass of a cubic foot of dry air ·0807 lb.

CHAPTER XXIV

ADIABATIC CHANGES AND CURVES

265. ADIABATIC CHANGES.—The changes that were considered in Chap. XXII as taking place in the volume and pressure of a gas took place slowly at constant temperature. In the operations considered in this chapter, pressure, volume, and temperature may all change simultaneously, but the condition is observed *that no heat enters or leaves the body during the operation.*

Although it is not possible experimentally to realize exactly the adiabatic conditions, they are often approximated to when the change takes place rapidly, and the substance acted on is surrounded by a bad conductor of heat.

The great change of temperature that often takes place under such conditions may be illustrated by a common experiment. A piston fits air-tight into a cylinder which contains air and a piece of tinder. On rapidly forcing down the piston the tinder is set on fire, showing that the air has been greatly heated. Where does this heat come from? By the light of the first law of Thermodynamics we are led to conclude that it is the equivalent of the work done by the external agent in forcing down the piston.

266. Steam.—If a mass of saturated steam be compressed adiabatically *the steam ceases to be saturated. Although its pressure is* considerably increased during the compression no water is formed, because the temperature is raised so much by the act of compression that the pressure attained is below the saturation pressure correspond-

ing to the new temperature. Thus to keep the steam saturated, heat must be withdrawn, when its pressure and temperature are increased. This result is sometimes expressed by the statement that the specific heat of saturated steam is negative.

267. ADIABATIC CURVES.—An adiabatic curve cannot be directly obtained as was the case with the isothermal (Art. 245). If it could be contrived that a mass of gas should be contained in a cylinder whose substance was a perfect non-conductor of heat, the relation between the volume and pressure could be obtained, and an adiabatic curve or line constructed in the same manner as in that article. Although this is not possible, the general form of an adiabatic curve can be readily shown. Let *nac* (fig. 180) be an isothermal line, and let us suppose a *quantity of gas contained* in a perfectly non-conducting cylinder to be in the condition corresponding to the point *a*, OF representing its volume and F*a* its pressure. Let the volume be adiabatically diminished to OG.

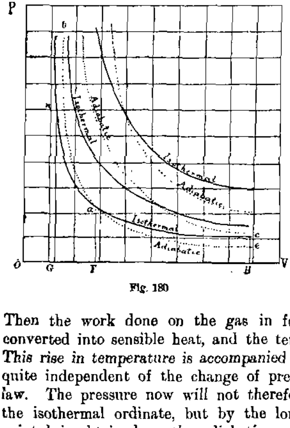

Fig. 180

Then the work done on the gas in forcing down the piston is converted into sensible heat, and the temperature of the gas rises. *This rise in temperature is accompanied by an increase of pressure* quite independent of the change of pressure indicated by Boyle's law. The pressure now will not therefore be represented by G*n*, the isothermal ordinate, but by the longer ordinate G*b*, and the point *b* is obtained on the adiabatic.

Let the gas be then restored to its original condition corresponding to the point *a*, and then let its volume be increased adiabatically to OH. The energy expended by the gas in forcing up the piston has for its equivalent the heat withdrawn from the gas, whose temperature therefore falls. The fall of temperature entails a fall of pressure, and the pressure now registered will be a quantity H*e* less than H*c*, and the *point e is obtained on the adiabatic.* Hence we see

that the adiabatic lines cut the isothermals in the way shown in fig. 180, the upper part of the adiabatic lying outside the isothermal, more remote from the line of zero pressure, the lower part inside, nearer to the line of zero volume. Fig. 180 shows three adiabatic and three isothermal lines for air. The isothermal lines are rectangular hyperbolas, the adiabatic lines are not of so elementary a geometrical nature.

268. EQUATIONS TO AN ADIABATIC CURVE.—Suppose a volume V of gas at pressure P, and temperature θ_1 to be enclosed in a perfectly non-conducting cylinder in which works a piston.

Let the gas be compressed adiabatically by an indefinitely small amount dV, and let the rise of temperature be $d\theta$; then the work done on the gas $= PdV$. Also the heat communicated to the gas is equal to C_v, the specific heat at constant volume multiplied by $d\theta$, the rise in temperature.

Then regarding the internal work as zero, if all the quantities be expressed in absolute units,

$$C_v \times d\theta = P(-dV),$$

the sign of dV being negative, because there is a diminution of volume.

Thus

$$C_v d\theta + PdV = 0 \quad \text{.......................(1)}$$

$$\text{but } P = R\theta \frac{1}{V}$$

$$\therefore C_v d\theta + R\theta \frac{dV}{V} = 0$$

$$\text{and } C_v \frac{d\theta}{\theta} + R \frac{dV}{V} = 0 \quad \text{.......................(2)}$$

Now every operation in which a gas is adiabatically compressed may be considered as divided into an indefinitely large number of successive operations, each indefinitely small. Equation (2) must therefore be integrated.

$$\therefore C_v \log_e \theta + R \log_e V = \text{a constant}$$

$$\text{But (Art. 257) } R = C_p - C_v = (\gamma - 1) C_v$$

$$\therefore C_v \log_e \theta + (\gamma - 1) C_v \log_e V = \text{a constant}$$

$$\therefore \log_e \theta + (\gamma - 1) \log_e V = \text{a constant}$$

$$\therefore \log_e \theta + \log_e V^{\gamma - 1} = \text{a constant}$$

$$\therefore \theta V^{\gamma - 1} = \text{a constant} \quad \text{.........(A)}$$

$$\text{or } \theta_1 V_1^{\gamma - 1} = \theta_2 V_2^{\gamma - 1} \quad \text{...........(A)}$$

An equation which shows the relation between volume and temperature when a gas is adiabatically compressed.

The relations between the pressure and temperature and between the pressure and volume may be obtained from equation (A) by remembering that under all circumstances the quantity $R' = \frac{PV}{\theta}$ remains constant. Thus $V = \frac{R\theta}{P}$, and equation (A) becomes

$$\theta_1\left(\frac{R\theta_1}{P_1}\right)^{\gamma-1} = \theta_2\left(\frac{R\theta_2}{P_2}\right)^{\gamma-1}$$

$$\therefore R^{\gamma-1}\frac{\theta_1^{\gamma}}{P_1^{\gamma-1}} = R^{\gamma-1}\frac{\theta_2^{\gamma}}{P_2^{\gamma-1}}$$

$$\therefore \left(\frac{\theta_2}{\theta_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1} \quad \text{......................(B)}$$

which shows the relation between the temperature and pressure.

Also since $\frac{\theta_2}{\theta_1} = \frac{P_2V_2}{P_1V_1}$

From equation (A) we have

$$\frac{\theta_2}{\theta_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = \frac{P_2V_2}{P_1V_1}$$

$$\therefore P_2V_2^{\gamma} = P_1V_1^{\gamma}$$

$$\text{or } PV^{\gamma} = \text{a constant}; \quad \text{..............(C)}$$

the equation which determines the nature of an adiabatic curve expressing the relation between pressure and volume.

269. WORK DONE DURING AN ADIABATIC CHANGE. —Let the original and final pressures and volumes be respectively P_1V_1 and P_2V_2.

Then in an indefinitely small change of volume dV the work done is

$$dW = P_1 dV$$

$$\text{But } P_1V_1^{\gamma} = P_2V_2^{\gamma} = PV^{\gamma} = \text{a constant A}$$

$$\therefore dW = A\frac{dV}{V^{\gamma}}.$$

And if W be the work done when the volume changes from V_1 to V_2,

$$W = A\int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$\text{Now} \int \frac{dV}{V^\gamma} = \frac{1}{\gamma - 1} \cdot \frac{1}{V^{\gamma-1}}$$

$$\therefore W = A\frac{1}{\gamma - 1}\left\{\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right\}$$

$$= \frac{PV^\gamma}{\gamma - 1}\left\{\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right\}$$

Or since $A = PV^\gamma = P_1V_1^\gamma = P_2V_2^\gamma$ the equation may be written

$$W = \frac{1}{\gamma - 1}\left\{\frac{P_1V_1^\gamma}{V_1^{\gamma-1}} - \frac{P_2V_2^\gamma}{V_2^{\gamma-1}}\right\}$$

$$= \frac{1}{\gamma - 1}\left\{P_1V_1 - P_2V_2\right\}\text{..................(D)}$$

If the expansion be to infinity we have

$$W = \frac{P_1V_1^\gamma}{\gamma - 1}\left\{\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right\}$$

and the last term becomes zero, whence

$$W = \frac{P_1V_1}{\gamma - 1}.$$

270. We proceed to an example. Two cubic feet of air at 0° C. under a pressure of 14·7 lb. per square inch are adiabatically compressed into 1 c. ft. Find the pressure and temperature momentarily attained, and the work done during the compression.

(*a*) Pressure.

$$P_1V_1^\gamma = P_2V_2^\gamma$$
$$\therefore (14{\cdot}7)(2)^{1{\cdot}41} = P_2(1)^{1{\cdot}41}$$
$$\therefore \log P_2 = \log 14{\cdot}7 + 1{\cdot}41(\log 2)$$
$$= 1{\cdot}1673 + 1{\cdot}41({\cdot}30103)$$
$$= 1{\cdot}5918$$
$$\therefore P_2 = 39{\cdot}066 \text{ (lb. per sq. in.)}.$$

(*b*) Temperature.

$$\theta_2V_2^{\gamma-1} = \theta_1V_1^{\gamma-1}$$
$$\theta_2(1)^{{\cdot}41} = 273(2)^{{\cdot}41}$$
$$\therefore \log\theta_2 = \log 273 + {\cdot}41(\log 2)$$
$$= 2{\cdot}43616 + {\cdot}12342$$
$$= 2{\cdot}55958$$
$$\therefore \theta_2 = 362{\cdot}7.$$

The rise of temperature is thus 89·7° C.

It is instructive to compare this result with that obtained in Examples 5 and 6 at the end of Chap. XXII. It might at first be supposed that the calculations in the latter of those examples gives the rise of temperature here required. But the work done on the gas in that case is less than when the compression takes place adiabatically. For the temperature commences to rise immediately the compression begins, and this rise of temperature increases the pressure of the gas, so that throughout this whole process the pressure to be overcome is greater than in the case of isothermal compression. We have therefore to employ greater force to effect the compression, and since this force works through the same distance as before, the work done is greater, and the rise of temperature must therefore be greater also.

(c) Work done.

$$W = \frac{1}{\gamma - 1}\{P_2V_2 - P_1V_1\}.$$

Since the pressures are now not on opposite sides of the equation, relative values are not sufficient; they must be expressed in terms of the square foot as V is expressed in cubic feet:

$$\text{Hence} \quad W = \frac{1}{\cdot 41}\{(144 \times 39\cdot066) - (144 \times 14\cdot7)2\}$$
$$= 2\cdot439 \times 144 \times 9\cdot666$$
$$= 3395 \text{ foot-pounds,}$$

which is equivalent in heat units to 2·44 pound-degrees.

Now suppose this energy to be expended in warming the air: then the mass of air = ·1614 lb., and the specific heat at constant volume = ·1685, whence the heat required to raise the air through 1° C. = ·1614 × ·1685 = ·0272 calorie.

The rise in temperature is therefore

$$2\cdot44 \div \cdot0272 = 89\cdot7^\circ \text{ C.,}$$

a result which agrees with that above.

271. ENTROPY.—Adiabatic curves are sometimes called **isentropics** or lines of constant entropy, just as isothermals are lines of constant temperature. The conception of entropy is much used in the mathematical treatment of thermal changes. It may be defined as that property of a substance which remains constant when a body assumes different states without gaining or losing heat. The entropy of a body increases when heat enters the body and decreases when heat leaves it.

If a body lose a quantity of heat H at a constant temperature θ_1 its entropy is diminished by an amount $\frac{H}{\theta_1}$; and if another body whose temperature is θ_2 receive this quantity of heat H, then its entropy is increased by the amount $\frac{H}{\theta_2}$.

The change of entropy in such an operation is therefore

$$\frac{H}{\theta_2} - \frac{H}{\theta_1} = H\frac{\theta_1 - \theta_2}{\theta_1\theta_2}.$$

This expression is positive, since θ_1 is greater than θ_2. There is therefore an increase of entropy. Heat always passes from a warmer to a colder body, and the entropy, therefore, of the universe is always increasing. When it has reached its maximum no more exchanges of heat can occur (Art. 211).

EXERCISES

1. A mass of air at 15° C. is suddenly compressed to half its volume. Calculate the temperature it will momentarily attain.

   log 2 = ·30103; log 1·32 = ·1204.

2. A mass of gas whose volume is 2 and pressure 5 is suddenly compressed until its volume is $\frac{4}{3}$. Find the pressure attained.

   log 5 = ·69897; log 3 = ·4771213
   log 4 = ·60206; log 7·5 = ·87506.

3. A mass of gas whose volume is 2 and pressure 5 expands adiabatically until its volume is 3. Find the pressure attained.

   log 2·82 = ·45607.

4. A cubic metre of air is under the normal pressure of 1·0333 kg. per sq. cm. By how much must the volume be increased in order that the pressure may be halved, the change taking place adiabatically?

   log 2 = ·30103; log 1·6349 = ·213496.

5. In the previous example find the temperature attained, if the gas were originally at 27° C.

   log 300 = 2·30103; log 163·49 = 2·2135.

6. Find the work done in Question 4.
7. A cubic foot of dry air at 17° C. is under a pressure of 14·7 lb. on the sq. in.; it is adiabatically compressed to four-fifths of a cubic foot. Find the pressure and temperature momentarily attained and the work done during the operation.

   log 14·7 = 1·167317; log 1·25 = ·09691
   log 20·135 = 1·3039604; log 290 = 2·462398
   log 317·78 = 2·502131.

8. Taking the equation $PV^{1\cdot41} = 10$, construct an adiabatic curve by giving P = successively the values 1, 2, 3, &c., and finding the corresponding values of V, and then taking the values of V as abscissæ and those of P as ordinates.

[*A table of logarithms will be required.*]

CHAPTER XXV

HEAT ENGINES

272. CONVERSION OF HEAT INTO MECHANICAL ENERGY.—The transformation of the energy of mechanical motion into heat is of very frequent occurrence; but the converse process, the conversion of energy from the form of heat to that of mechanical motion, can only be effected in a very limited number of ways. It may be accomplished by heating a thermo-electric junction and utilizing the electric current thus produced to drive an electromagnetic engine, or by taking advantage of the expansion produced when substances are heated. Any contrivance by which heat is continuously converted into work is called a heat engine, the exact mode in which this is effected being a matter of practical convenience and not of principle. Of heat engines based on the principle of expansion the forms in most general use are air engines, gas engines, and steam engines. Engines can be constructed in which the "working substance" is and remains solid or liquid, but they are not economical on account of the small coefficients of expansion of solids and liquids. In the case of the steam engine the heat effects the vaporization of the water and thereby produces a very great increase of volume if the pressure remain constant. We proceed to examine the essential parts of one or two simple forms of engine before approaching the theory of such engines.

273. THE STEAM ENGINE.—Fig. 181 illustrates the fundamental principles of the steam engine. The steam is generated in a boiler M, and passes thence into a cylinder where the steam does its work on a piston P, and I is a condenser to which it then passes, and where by means of a spray of cold water it is condensed. In the double-acting engine the pipes are arranged as shown, the boiler and condenser each having means of free communication with both sides of the piston, but the mechanism is such that when the piston is descending the stopcocks *a* and *c* are open and *b* and *d* are closed;

and when the piston is ascending *b* and *d* are open but *a* and *c* are closed. By means of the beam GE pivoted at O, the piston P communicates motion to the driving rod GL that turns the wheel R.

The piston being at the bottom of the cylinder, suppose the stopcocks *b* and *d* to be opened while *a* and *c* are closed; steam from the boiler enters the cylinder at the bottom and forces up the piston. When or before the piston has reached the top of the cylinder the stopcocks *b* and *d* are closed and *a* and *c* opened; the steam from the boiler then enters the cylinder at the top and forces the piston down. At the same time the steam in the lower part of the cylinder is

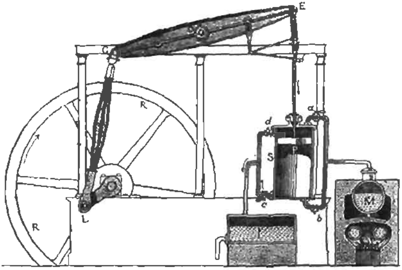

Fig. 181

rapidly lowered in pressure and soon condensed into water by its communication with the cold condenser. Thus one side of the piston is in communication with the boiler where the steam is at a higher pressure, and the other side with the condenser where the steam is at a much lower pressure, and by the alternation of these conditions the piston is made to move up and down. If the condenser could be made to effect the condensation of the steam instantaneously and completely there would always be a vacuum on one side of the piston. Since this is not practicable there is always some pressure of steam against the motion of the piston.

Owing to the high latent heat of steam the water in the condenser gets heated, and it is necessary therefore to have in communication with the condenser a continuous and abundant supply of cold water. When the water has become thus heated it may with advantage be allowed to flow into the boiler, instead of supplying that with cold water.

274. STIRLING'S AIR ENGINE.—The *construction* of Stirling's engine may be understood by reference to fig. 182. AA is a cylinder having a double bottom, the inner one being perforated with numerous holes. In this works a large closely-fitting hollow metal plunger PP, of which the lower part B is filled with brick dust

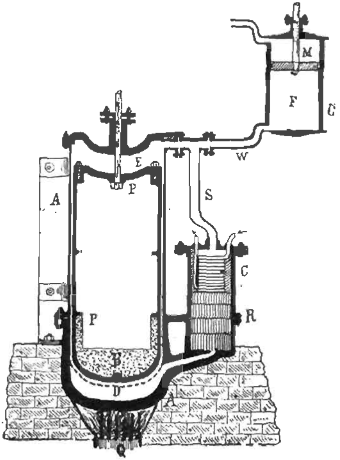

Fig. 182

or other bad*ly-conducting material.* The top and bottom of the *cylinder* A *are connected through a tube or box* R *called the regenerator, and the upper portion* E *of the cylinder also communicates* with the working cylinder G in which moves the piston M.

The regenerator R consists of a number of very thin strips of sheet iron arranged side by side about $\frac{1}{50}$ of an inch apart so as to expose a very large surface; and at the top of these is a coiled copper pipe C through which when the machine is at work a stream of cold water is maintained by a pump.

The substance occupying the spaces EDF and the tubes connecting them is compressed air, which is heated by a flame Q.

When the engine has been at work for some time so that its parts have reached a permanent condition as to temperature, the bottom of the regenerator R, which is near the flame, is at a high temperature, while the top is kept cool by the water circulating in the coils C, so that there is a gradually decreasing temperature from the bottom to the top, and the air as it passes through the regenerator changes its temperature gradually. In fact its temperature never differs much from the metallic surface with which it is in contact, and between which and itself a constant interchange of heat is going on.

The method of working is as follows:—

Suppose the plunger P to be originally at its lowest position and then to rise; air is forced out of the space E and passes through R to the space D. This air takes up some heat as it passes through the regenerator, and more still when in the hot chamber D; its pressure consequently increases greatly, and this increased pressure is communicated to the air in the tubes S, W, and the cylinder G, and causes the piston M to rise. When the plunger P descends the hot air leaves the chamber D and, passing through the regenerator, becomes cooled as it goes; its pressure is consequently diminished and the piston M descends. The two pistons are so connected that one is half a stroke in front of the other.

The upper portion of the cylinder G is connected with an arrangement exactly like that described; and matters are so contrived that the maximum pressure on one side of the piston M coincides with minimum pressure on the other side. There is pressure on both sides of the piston, and the working force is the difference between them.

275. **Function of the Regenerator.**—Since no external work is done when heat passes by conduction from one substance to another, it is necessary, in order that an engine may have a high efficiency, that such a process should be avoided, i.e. the working substance should be as nearly as possible at the same temperature as the source when it takes in the heat and at the same temperature as the refrigerator when it gives out the heat.

The function of Stirling's regenerator is to effect this object as nearly as possible.

276. PARTS OF A HEAT ENGINE.—We have now examined briefly two types of heat engines. The gas engine involves

no new principles. From the above sketches an idea may be obtained of the parts and method of working of any heat engine, which may be thus summarized.

(i) In every heat engine there must be a furnace or source of heat, and a refrigerator or condenser into which the working substance passes when its work is done. No form of heat engine exists in which the working substance does not take in heat from some source at a higher temperature, and give out heat at a lower temperature.

The expression of this experimental fact is the second law of Thermodynamics (see Chap. XXVI).

(ii) The nature of the working substance is not of the essence of the problem. It may be solid, liquid, or gaseous, the one necessary condition being that it must change its volume when heated. As a matter of practical convenience a gas or vapour is best.

(iii) In order that the process may go on continuously there must be a reciprocating motion of the piston, and a constant recurrence of the same series of stages.

This is called a **cycle** of operations.

277. WORK DONE. THE INDICATOR.—The work done by an engine may be ascertained from information obtainable from the engine itself. Thus, to consider only a single stroke of the piston; it moves a certain distance against a certain force, and the work done during that stroke is equal to the product of the total mean pressure on the piston by the length of the stroke. The work done in any given time is then obtained by multiplying this result by the number of strokes of the piston completed in the time.

The measurement is effected by an indicator. Richard's indicator is shown in fig. 183, by means of which a diagram is traced on a sheet of paper. The paper is rolled on a cylinder GH which can rotate round a vertical axis, and the diagram is traced out by a pencil P. The cylinder GH is geared to the piston of the engine in such a manner that as the piston moves to and fro the cylinder turns once round and back.

The pencil P is carried by the middle one of three levers which are fastened at the points A and C to external supports. The lever CD is connected with a piston F which works in a cylinder Z, and the particular arrangement of levers adopted causes the pencil P to move up and down in a vertical line as the piston F moves up and down in the cylinder. The movements of the piston F are controlled by a strong spring which presses against its upper surface.

The lower part of the cylinder Z communicates with the cylinder of the steam engine by a pipe, and the under side of the piston is therefore subjected to a pressure which is always the same as that in the cylinder of the engine. As this pressure increases or diminishes the spiral spring is compressed or extended, and this compression or extension is proportional to the pressure on the piston. The position of the point of the pencil P in a vertical line thus indicates at any moment the pressure on the piston of the engine.

The numerical relation between the movement of the pencil and the corresponding change of pressure evidently depends on

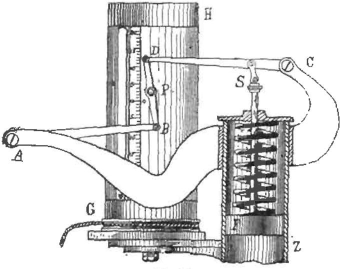

Fig. 183

the elasticity of the spring, the length of the levers, &c., and is for each instrument determined beforehand by a series of experiments in which the pressure is known, and the movement of the pencil observed.

Similarly the relation between the actual length of stroke of the piston of the engine and the distance passed over by any fixed point on the cylinder GH must be independently known.

278. Indicator Diagram.—If the cylinder GH be connected with the piston of the engine while Z is still unconnected with the steam chamber, the pencil remains at rest while the paper rotates, and there is marked out on the cylinder GH a horizontal line, the line of no pressure. If the cylinder GH remain unconnected with the piston of the engine and therefore at rest, while Z is placed in connection with the steam chamber, the pencil moves up and down, and traces

out a vertical line. If GH be connected with the piston and Z with the steam chamber simultaneously, the line traced out by the pencil under the combined motions is a curve. If the action of the engine is uniform, the curve traced out by each complete stroke is the same, and its area represents the work done during the stroke. Let us consider one complete stroke of the piston. When the boiler is placed in communication with the cylinder the pressure rises to a certain value indicated by the point *a* (fig. 184), and the piston moves forward under this pressure through a length represented by the line *ab*, which, if the pressure remain constant throughout the whole stroke, is a straight line parallel to OV. The work done during this forward stroke being the product of force by distance is represented by the rectangle *abc*O. When the forward stroke is ended, the steam is got rid of, and the pressure on this side of the piston is at once reduced, but generally has an appreciable value that may be represented by the line *ce*. The backward motion of the piston is opposed by this pressure, and the work done against it is represented by the rectangle *ec*O*f*. The total work therefore done during the complete stroke is represented by the area *abef*.

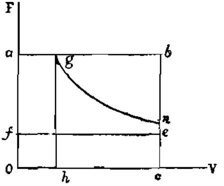

Fig. 184

The above diagram evidently represents the conditions under which the maximum rate of working is obtained from the engine. But it is uneconomical to allow the steam to escape at full pressure. The communication between the boiler and the cylinder is therefore cut off before the piston has finished its forward stroke, and the remainder of the stroke is accomplished under the gradually diminishing pressure of the expanding steam that has already been admitted into the cylinder. The diagram then takes the form *agnc*O, the curve *gn* showing the relation between the pressure and volume of the steam during the variable period.

The area *ghcn* may be found by the method of Art. 252. In practice it is usually found by drawing a large number of ordinates, and finding the areas of a number of small rectangles whose heights are the ordinates thus drawn, or by the planimeter.

The "effective pressure" on the piston at any moment is equal

to the difference between the pressures on its two sides. The mean effective pressure is the mean of such values. It corresponds to the mean ordinate on the diagram. When the mean effective pressure is known, the product of this into the length of the stroke gives the work done during the stroke.

279. EFFICIENCY OF ENGINES.—*Calculations made on the above principle give the indicated horse-power of an engine.*

The brake horse-power, i.e. that which the engine actually gives out to machinery, is less than the above, owing to loss of energy by conduction, radiation, and friction of the moving parts.

It has been shown in Chapter XV how the number of units of energy (H) evolved during the combustion of unit mass of coal may be ascertained.

The indicator diagram enables us to determine the quantity of work W done by the engine during the combustion of this quantity of coal.

The ratio $\frac{W}{H}$ *is called the efficiency of the engine. The quantities* H and W must, of course, be measured in the same units.

For ordinary engines this ratio is small, *the loss of energy that takes place from various causes being very large.*

280. EXAMPLES.

1. The area of the piston of a steam engine is 200 sq. in., length of stroke 3 ft., the average pressure behind the piston is 25 lb. per sq. in. greater than that in front of it, and the number of double strokes per minute 50. Find the horse-power at which the engine is working. If the engine consumes 300 lb. of coal per hour and the heat generated by the combustion of 1 lb. of coal is 8600 pound-degrees, how much per cent of the heat generated in the furnace is converted into useful work?

Work done in one stroke = 200 × 25 × 3 foot-pounds.

" " minute = 1500000 " "

$\therefore$ Horse-power $= \frac{1500000}{33000} = \frac{500}{11} = 45{\cdot}45.$

Coal consumed in one minute = 5 lb.

$\therefore$ Heat generated " = 43000 pound-degrees.

Work equivalent of this = 43000 × 1390 foot-pounds.

$\therefore$ Percentage of heat utilized $= 100 \times \frac{1500000}{43000 \times 1390} = \frac{15000}{43 \times 139} = 2{\cdot}5.$

2. A weight of 6 tons is dragged for a length of 330 ft. up a rough plane inclined 30 degrees to the horizontal, the coefficient of friction being $\frac{1}{\sqrt{3}}$. How many pounds of coal must be burned to effect this in an engine whose efficiency is 10 per cent?

Work done—

(*a*) In dragging the weight along the base of the plane

$$= 8 \times 2240 \times 165\sqrt{3} \times \frac{1}{\sqrt{3}} \text{ foot-pounds.}$$

(*b*) In raising the weight through the height of the plane

$$= 8 \times 2240 \times 165 \text{ foot-pounds.}$$

$$\therefore \textit{Total work} \text{ done} = 330 \times 17920 \text{ foot-pounds}$$
$$= 5913600 \text{ foot-pounds}$$
$$= 5913600 \div 1390 = 4254 \text{ pound-degrees.}$$

(*c*) ∴ Heat produced in engine = 42540 pound-degrees;

which is supplied by $\frac{42540}{8600} = 4{\cdot}94$ lb. of coal.

3. What is the efficiency of an engine which consumes 28 lb. of coal in drawing a train 1 mile against a resistance equal to the weight of $1\frac{1}{2}$ ton, the calorific power of the coal being such that the combustion of 1 lb. furnishes 8576 units of heat.

(1) Work done by the engine while running 1 mile

$$= 1\tfrac{1}{2} \times 2240 \times 1760 \times 3 \text{ foot-pounds.}$$

(2) Energy given out by the coal

$$= 28 \times 8576 \times 1390 \textit{ foot-pounds.}$$

$$\therefore \text{Efficiency} = \frac{3 \times 2240 \times 1760 \times 3}{2 \times 28 \times 8576 \times 1390}.$$
$$= {\cdot}053, \text{ i.e. } 5{\cdot}3 \text{ per cent.}$$

EXERCISES

1. A piston whose area is 115 sq. in. has a length of stroke 4 ft.; the effective pressure being 15 lb. on the sq. in., find the work done in one stroke.
2. A piston whose area is 96 sq. in., and length of stroke 3 ft., works with an effective pressure of 25 lb. per sq. in. on the piston. If the horse-power developed be 10, how many strokes per minute are made by the piston?
3. In a steam engine the diameter of the steam cylinder is 50 in., the length of stroke is 7 ft., the number of double strokes is 25 per minute, and mean effective pressure of the steam is 11·3 lb. on the sq. in. Find the horse-power of the engine.
4. The cylinder of an engine is 25 in. long; steam is admitted at 18 lb. actual pressure until one-fourth of the stroke is completed, and the final pressure is 4 lb. Dividing the stroke into 10 equal parts, find the steam pressure at each point of division, and set out a diagram of the work done. Find also the mean pressure of the steam.
5. The cylinders of a locomotive engine are 17 in. in diameter, and the length of stroke is 24 in.; also, the driving wheel makes 100 revolutions (double strokes) per minute, and the mean effective pressure of the steam is 80 lb. Find the horse-power.
6. An engine is competent to raise 70 millions of pounds through 1 ft. by the burning of 112 lb. of coal. How many pounds of coal does it consume per horse-power per hour?

7. Define the horse-power of an engine. If an engine consumes 2 lb. of coal per horse-power per hour, how many foot-pounds of work will it perform when consuming 112 lb. of coal?
8. Find the horse-power of a locomotive engine which can draw a train weighing 100 tons (including its own weight) along a level road at 30 miles per hour, the train resistance being taken at 10 lb. per ton of load.
9. If 400 tons be lifted 10 ft. in 10 min. by a steam engine, of which the area of the piston is 400 sq. in., the mean pressure of the steam on the piston 25 lb. on the sq. in., the length of stroke 4 ft., and the number of double strokes made in a minute 15, what proportion of the power applied to the piston is lost in the working of the machinery?
10. The diameter of the cylinder of an engine being 53 in., the stroke 5 ft., and the number of revolutions 30 per min., find the mean pressure of the steam to develop 600 indicated horse-power.
11. What is the amount of work done in a single stroke by an engine when the average working pressure of the steam is 20 lb. weight per sq. in., the length of the stroke 2 ft., and the diameter of the piston 7 in.?

CHAPTER XXVI

THEORY OF HEAT ENGINES

281. CARNOT'S PERFECT ENGINE. — In the preceding chapter some idea has been given of the principles of working of actual heat engines. The main process on which our attention is fixed is a conversion of heat into work. Whether steam, coal gas, or air be employed as the "working substance" is merely a matter of convenience of application—not a matter of fundamental principle. Steam is widely used merely because it is a convenient substance for carrying the energy and applying it as desired. In thermodynamics we think only of the quantities of energy that these working substances take in and give out. We therefore proceed to consider the theory of heat engines without regard to the practicability of the arrangements. To illustrate these principles, Carnot, a French engineer, put forth the idea of a very simple engine. No such engine can be actually made; it is imagined and described only to enable us to consider the essential operations free from confusing practical details. In fig. 185 A represents the source of heat, a body always maintained at a higher temperature θ_2; X represents the refrigerator, a cold body maintained at a constant lower temperature θ_1; C is a cylinder, containing the working substance confined by a piston P. The sides of this cylinder and the

piston are *perfect non-conductors* of heat; the bottom of the cylinder is a *perfect conductor*. N is a stand also of perfectly non-conducting material.

Such an engine is called a perfect engine, because no energy is lost by friction, conduction, or radiation, and no portion of the working substance escapes from the machine in an unknown condition.

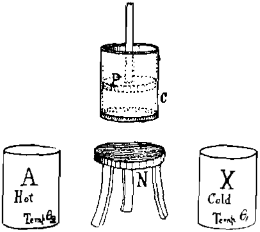

Fig. 185

The working substance starts in a certain known state, and after going through a set of operations, leaves off in exactly the same condition as that in which it started. Under these circumstances there is no change in the intrinsic energy of the working substance, which merely serves as a carrier by which energy is taken from one body and given to another, itself being in the result unaffected. Such a set of operations is called a *cycle* or sometimes a *complete cycle*. We proceed to trace such a cycle on an indicator diagram.

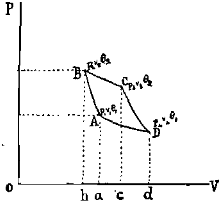

Fig. 186

282. CYCLE OF OPERATIONS. — Suppose the working substance to be originally at the temperature θ_1 of the refrigerator, and let its condition as to volume (V_1) and pressure (P_1) be represented by the point A on the indicator diagram (fig. 186). Then let the substance pass through a cycle of changes, thus:—

(i) Let the cylinder be placed on the non-conducting stand, and by forcing the piston down, let the substance be compressed till its temperature has risen to θ_2 that of the source, and let its volume then be V_2, and its pressure P_2. To effect this compression external work has to be *done upon* the substance, the amount (W_1) of this work being represented by the

area *ABba*. Since no heat enters or leaves the substance during the operation, *the path* AB *is a portion of an adiabatic line.*

(ii) Let the cylinder now be placed in contact with the source, and let the piston slowly rise till the volume of the working substance be V_3 and the pressure P_3 corresponding to the point C on the diagram, the temperature remaining constant during the process. To maintain the temperature constant, a quantity of heat H passes from the source into the working substance; and since the piston, which exerts a pressure on the substance, has moved upward, a quantity of external work W_2, represented by the area *BCcb*, has been *done by* the substance. *Since the temperature during the process* has remained constant, the path BC is a part of an isothermal line.

(iii) Let the cylinder now be placed on the non-conducting stand, and let the working substance expand. During this process the temperature of the substance gradually falls, and the process is discontinued when the temperature has fallen to θ_1 that of the refrigerator, the volume then being V_4 and the pressure P_4 corresponding to the point D on the diagram. In this stage a quantity W_3 of external work represented by the area *CDdc* has been *done by* the working substance; and since no heat has entered or left the substance, the path CD is part of an adiabatic line.

(iv) Let the cylinder be placed in contact with the refrigerator, and let the piston be slowly forced down until the volume has diminished to its original volume V_1 and the pressure increased to its original value P_1 corresponding to the point A on the diagram, *so that the working substance is now in the same condition as at* first. To effect this compression external work has to be *done upon* the substance, the amount W_4 of this work being represented by the area *DAad*. The effect of the compression would be to heat the substance were it not that this heat, whose amount is *h*, escapes to the refrigerator, and the temperature therefore remains constant at θ_1, so that the line DA on the diagram is part of an isothermal.

283. WORK DONE DURING THE CYCLE.—During the cycle a quantity of work $-W_1 + W_2 + W_3 - W_4 = W$, represented by the area ABCD, has been done by the engine; a quantity of heat H has been taken from the source and a quantity *h* has been given to the refrigerator. Since the substance is in exactly the same state at the end as at the beginning of the cycle no other quantity of energy can be concerned in the operation,

and we have therefore by the first law of Thermodynamics the equation

$$W = H - h,$$

or the work done is the mechanical equivalent of the difference between the quantity of heat taken from the source and that given to the refrigerator.

Carnot's view was that heat, being a material substance, could not be destroyed or transformed to something else, and therefore that H was equal to h—i.e. all the heat taken from the source was given to the refrigerator. The work W he conceived to be due to the fall of a quantity of heat H from a higher temperature θ_2 to a lower temperature θ_1, just as a mass of water will do work in falling from a higher to a lower level without any diminution in the quantity of water. But there is no ground for supposing that a quantity of heat in a hotter body contains more energy than the same quantity existing in a colder body; and, moreover, Carnot's view must be incorrect, as appears from the following considerations:—

(i) When heat passes by conduction from a hot body to a cold one, the amount of heat received by the cold body is admittedly equal to that emitted by the hot body; but in this case no external work is done. Hence it would appear that a quantity of this material fluid called caloric, in falling through a range of temperature, may in one case do external work and in another case not, which is improbable.

(ii) Joule's experiments show that we might employ the engine in heating water, and thus from the work W we could get more heat, a consideration which renders it impossible that H should equal h.

(iii) Hirn, by experiments on the steam engine, has shown numerically that H is greater than h. (Art. 217.)

284. REVERSIBILITY.—The set of operations indicated in Art. 282 can be reversed, and the same diagram will be traced out in the reverse direction. Suppose the body to be in the state corresponding to the point B (fig. 186) and the cycle to be performed in an anti-clockwise direction.

(i) The cylinder being placed on the non-conducting stand, the substance is allowed to expand along the adiabatic from the state corresponding to the point B to the state corresponding to the point A. During this process it does work W, but receiving no heat, its temperature falls from θ_2 to θ_1.

(ii) The cylinder being placed in contact with the refrigerator, the substance is allowed to expand along the isothermal AD, taking in a quantity of heat h, and maintaining its temperature constant at θ_1.

(iii). The cylinder being placed on the non-conducting stand, the substance is compressed without loss of heat, its temperature rising to θ_2, and the path traced out being the adiabatic line DC.

(iv) The substance while in contact with the source is then further compressed, during which process it gives out heat H to the source, and its temperature θ_2 remaining constant, the path traced out is the isothermal CB.

The working substance has now returned to its original condition; the path traced out has been *reversed*, and *work has been done on the substance*. The main difference between the operations may be thus presented:—

Direct Operation.	*Reversed Operation.*
The working substance receives a quantity of heat H from the source, and gives out a smaller quantity h to the refrigerator. The quantity of heat $H - h$ is converted into work W done by the engine.	The working substance receives a quantity of heat h from the refrigerator and gives out a larger quantity H to the source. The work W done on the engine is converted into a quantity of heat $H - h$.

In the reversed operation heat is transferred from a colder to a hotter body, *but to accomplish this an expenditure of work is necessary*.

285. **Conditions of Reversibility.**—In order that an engine may be reversible it must fulfil these conditions:—

(i) No heat must be spent in overcoming friction, or lost by radiation or conduction, or changed into magnetic or electric energy.

(ii) The changes of pressure and volume must take place very slowly, so that while heat is being taken in or given out the temperature of the working substance at any moment may differ only infinitesimally from that of the source or refrigerator with which it is in contact.

In the cycle of operations of Carnot's engine described above, the temperature of the working substance was brought to that of the source and refrigerator respectively before the substance was placed in contact with them. It is essential to the theory of a perfect heat engine that the heat be taken in and given out at a constant tempera-

ture. In Stirling's engine it is the function of the regenerator to ensure, as far as may be, that when the hot air reaches the source and refrigerator respectively it is already raised or lowered in temperature to the required extent.

Expansion and contraction of gases, evaporation and liquefaction are instances of reversible processes. How these processes afford examples of perfect heat engines is considered in Chap. XXVII. Many natural processes are not reversible, and such irreversible processes are not examples of perfect heat engines.

286. CARNOT'S PRINCIPLE.—The efficiency of an engine has been already defined (Art. 279). Carnot's principle is that the test of maximum efficiency is reversibility, that "the efficiency of a reversible engine is the greatest that can be obtained with a given range of temperature". The truth of the principle is demonstrated as follows: Let X be a reversible engine, and (if possible) let Z be an engine more efficient than X, then this means that the ratio $\frac{W_1}{H_1}$ for Z is greater than the same ratio $\frac{W_2}{H_2}$ for X, i.e. $\frac{W_1}{H_1} > \frac{W_2}{H_2}$, and if H_1 be equal to H_2, then $W_1 > W_2$.

Let then the engines be coupled inversely and work with the same source and refrigerator, then the engine Z restores to the source the heat H_1 taken from it by the engine X, while external work of the amount $W_1 - W_2$ is done. This work then must be done by heat derived from the refrigerator, and *it is contrary to all experience that work should be obtained continuously by abstracting heat from the refrigerator of an engine.* The principle is therefore subject to the truth of the statement italicized. Assuming this, it follows that for any assigned temperature limits the efficiency is a maximum when the engine is reversible, and that all reversible engines working between those limits have the same efficiency.

287. **Expression for Efficiency. Carnot's Function.** —When work is done by a perfect engine a quantity of heat passes between two bodies at different temperatures. If the two bodies are of the same temperature no work is obtained. If work is obtained, the temperatures must be different. No external body is present with which any interchange of energy can take place, and the working substance leaves off in the possession of as much energy as it started with.

Moreover the nature of the source and refrigerator do not enter into the argument, nor does the particular nature of the reversible

process employed—it is sufficient that it be reversible. The quantity of heat transferred in the cycle can thus only depend on the thermal conditions (i.e. the temperatures) of the source and the refrigerator. Let these be respectively θ_2 and θ_1; then the efficiency may be written equal to A $(\theta_2 - \theta_1)$ where A is some function of the temperature. The quantity A is called *Carnot's function*. We proceed to indicate what the value of A must be.

Consider the cycle of an engine in which the working substance is a perfect gas. Then in the states corresponding to the points A, B, C, D, fig. 186, respectively, we have—

$$\frac{P_1V_1}{\theta_1} = \frac{P_2V_2}{\theta_2} = \frac{P_3V_3}{\theta_2} = \frac{P_4V_4}{\theta_1} = R.$$

The work done during the change along the adiabatic AB is by Art. 269.

$$W_1 = \frac{1}{\gamma - 1}\{P_1V_1 - P_2V_2\}$$
$$= \frac{1}{\gamma - 1}R\{\theta_1 - \theta_2\}.$$

The work done during the change along the adiabatic CD similarly is—

$$W_3 = \frac{1}{\gamma - 1}\{P_3V_3 - P_4V_4\}$$
$$= \frac{1}{\gamma - 1}R\{\theta_2 - \theta_1\}.$$

These changes being of opposite sign and equal in quantity cancel each other.

The work W_2 done by the gas during the change along the isothermal from B to C is equal to the heat absorbed during the change. Hence by Art. 252—

$$W_2 = H = P_2V_2 \log_e \frac{V_3}{V_2}$$
$$= R\theta_2 \log_e \frac{V_3}{V_2}.$$

The work W_4 done on the gas during the change along the isothermal from D to A similarly gives—

$$W_4 = h = R\theta_1 \log_e \frac{V_4}{V_1}.$$

But since AB and CD are adiabatic lines, we have by equation (A) (Art. 268)—

$$\theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1}$$

and $$\theta_1 V_4^{\gamma-1} = \theta_2 V_3^{\gamma-1}.$$

Whence $$\frac{V_3}{V_2} = \frac{V_4}{V_1} \text{ and } \log\frac{V_3}{V_2} = \log\frac{V_4}{V_1}$$

$$\therefore \frac{W_2}{W_4} = \frac{H}{h} = \frac{R\theta_2 \log\frac{V_3}{V_2}}{R\theta_1 \log\frac{V_4}{V_1}} = \frac{\theta_2}{\theta_1}$$

$$\therefore \frac{W_2 - W_4}{W_2} = \frac{H-h}{H} = \frac{W}{H} = \frac{\theta_2 - \theta_1}{\theta_2} \text{.......(E)}$$

and $$\frac{W_2 - W_4}{W_4} = \frac{H-h}{h} = \frac{\theta_2}{\theta_1} - 1.$$

Now $\frac{W}{H}$ is the ratio between the work done by the engine and the energy it absorbs from the source, which is the definition of efficiency.

$$\therefore \text{Efficiency} = \frac{\text{Difference of temperature between source and refrigerator}}{\text{Temperature of source}}.$$

Carnot's function A is thus shown to be equal to $\frac{1}{\theta_2}$, i.e. the reciprocal of the absolute temperature of the source.

The total work done by the gas

$$= W = W_2 - W_4 = R\left(\theta_2 \log\frac{V_3}{V_2} - \log\frac{V_4}{V_1}\right)$$

$$= R \log\frac{V_4}{V_1}(\theta_2 - \theta_1)\text{.....................(F)}$$

288. As an example we take a pound of air round a Carnot's cycle, between the temperatures 0° C. and 100° C.

Referring to fig. 186—

Point A.—Let $\theta_1 = 273$ (0° C.): $P_1 = 2117$ lb. per. sq. ft., then $V_1 = 12{\cdot}39$ c. ft.: $R = 96{\cdot}1$.

The first operation is an adiabatic compression along the line AB, then (Art. 268)—

$$\theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1}$$

$$\therefore 273(12{\cdot}39)^{\cdot 41} = 373(V_2)^{\cdot 41}$$

$$\text{whence } V_2 = 5{\cdot}793.$$

$$\text{Also } P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\therefore (2117)(12{\cdot}39)^{1\cdot 41} = P_2(5{\cdot}793)^{1\cdot 41}$$

$$\text{whence } P_2 = 6183{\cdot}8.$$

Also work done (Art. 269) $= W_1 = \frac{1}{\gamma - 1}\{P_1V_1 - P_2V_2\}$

$$= \frac{1}{\gamma - 1} \cdot R \cdot (\theta_1 - \theta_2)$$

$$= \frac{1}{\cdot 41} \times 96{\cdot}1 \times (-100)$$

$$= -23439 \text{ foot-pounds.}$$

Point B on the diagram has been reached where

$$\theta_2 = 373 : P_2 = 6183{\cdot}8; \; V_2 = 5{\cdot}793.$$

The second operation is an isothermal expansion along the line BC. Let it continue till, say, $V_3 = 1{\cdot}5\ V_2 = 8{\cdot}689.$

$$\text{Now } P_3V_3 = R\,\theta_2$$

$$\therefore 8{\cdot}689\ P_3 = 96{\cdot}1 \times 373$$

$$\therefore P_3 = 4125.$$

Also work done (Art. 252) $= W_2 = R\,\theta_2 \times 2{\cdot}3026 \times \log \frac{2}{3}$

$$\therefore W_2 = 35845{\cdot}3 \times 2{\cdot}3026 \times (-{\cdot}176091)$$

$$= -14534 \text{ foot-pounds.}$$

Point C on the diagram has been reached where

$$\theta_2 = 373 : P_3 = 4125; \; V_3 = 8{\cdot}689.$$

The third operation is an adiabatic expansion along the line CD till the temperature falls to 0° C., then—

$$\theta_2 V_3^{\gamma - 1} = \theta_1 V_4^{\gamma - 1}$$

$$\therefore 373(8{\cdot}689)^{\cdot 41} = 273\ V_4^{\cdot 41}$$

$$\therefore V_4 = 18{\cdot}584.$$

$$\text{Also } P_4 = R\,\theta_1 \div V_4$$

$$= 96{\cdot}1 \times 273 \div 18{\cdot}584$$

$$= 1411{\cdot}7.$$

Also work done—

$$= W_3 = \frac{1}{\gamma - 1} \cdot R \cdot (\theta_2 - \theta_1)$$

$$= \frac{1}{\cdot 41} \times 96{\cdot}1 \times 100$$

$$= 23439 \text{ foot-pounds.}$$

Point D on the diagram has been reached where

$$\theta_1 = 273 : P_4 = 1411{\cdot}7; \; V_4 = 18{\cdot}584.$$

The fourth operation is isothermal compression at 0° C. along the line DA till

$$V_1 = 12 \cdot 39.$$

$$\text{Since } P_4V_4 = P_1V_1$$

$$1411 \cdot 7 \times 18 \cdot 584 = 12 \cdot 39\ P_1$$

$$\therefore P_1 = 2117.$$

Also work done (Art. 250)—

$$= W_4 = R\,\theta_1 \times 2 \cdot 3026 \times \log_{10} \frac{18 \cdot 584}{12 \cdot 39}$$

$$= 96 \cdot 1 \times 273 \times 2 \cdot 3026 \times \cdot 176091$$

$$= 10637 \cdot 5 \text{ foot-pounds.}$$

Point A on the diagram has been reached where

$$\theta_1 = 273 : P_1 = 2117;\ V_1 = 12 \cdot 39,$$

and the air is in its original condition.

The work done on the air is the sum of the amounts done in the separate operations—

$$W = W_1 + W_2 + W_3 + W_4$$

$$= -23439 - 14534 + 23439 + 10637 \cdot 5$$

$$= -3896 \cdot 5 \text{ foot-pounds;}$$

i.e. the work done *by* the air is 3896·5 foot-pounds.

The amount of work done W is represented by the area ABCD, and may be calculated from equation (F) above.

$$\therefore W = R \log \frac{V_4}{V_1} (\theta_2 - \theta_1)$$

$$= 96 \cdot 1 \times \log_{10} \tfrac{3}{2} \times 2 \cdot 3026 \times 100$$

$$= 3896 \cdot 5,$$

which agrees with the result obtained from an examination of the detailed operation.

In the above demonstration we have supposed the working substance to be a perfect gas. But the arguments of Arts. 281 to 286 are general, and it is shown that whatever the working substance may be, provided that it is taken round a reversible cycle, any other reversible engine has the same efficiency. Equation (E) above is therefore of universal application. And it is of great practical importance, for it shows the limits within which improvements in actual heat engines are possible. A perfect engine working within ordinary limits of temperature rejects the greater part of the heat supplied to

it, and no real engine can be made perfect. The efficiency of heat engines must therefore be low. As the conditions laid down in Art. 285 are more closely fulfilled the nearer will an actual engine approach the efficiency of a perfect engine.

289. ABSOLUTE TEMPERATURE.—The absolute temperatures hitherto mentioned have been considered as obtained from the indications of a gaseous thermometer, the gas being a perfect gas. Lord Kelvin took the expression for the efficiency of a heat engine as the basis of a scale of temperature. This scale is usually meant when the absolute scale of temperature is spoken of, because it is independent of the behaviour of any particular substance.

In Art. 287 it was shown that if a working substance be taken round a reversible cycle, then

$$\frac{H}{h} = \frac{\theta_2}{\theta_1}.$$

Lord Kelvin therefore proposed to construct a scale of temperature by making "the absolute values of two temperatures in the ratio of the heat taken in to the heat rejected in a perfect thermodynamic engine working with a source and refrigerator at the higher and lower of the temperatures respectively", so that "a unit of heat descending from a body A at the temperature θ on this scale, to a body B at temperature $\theta - 1$ would give out the same mechanical effect whatever be the value of θ".* If we then imagine an engine whose efficiency is unity, i.e. one which converts all the heat it receives into work, the refrigerator of such an engine must be at absolute zero. The nearest practical realization of this scale is that obtained from a reversible engine in which the working substance is one of the more perfect gases, and from the experiments on those substances related in Art. 242, Lord Kelvin determined to what extent those gases differed from the ideal perfect gas, and how far such difference of constitution tended to produce divergence between the absolute scale of temperature and the scale of the gas thermometer. His conclusion from the most accurate experiments on air and hydrogen was that if the temperature difference between 0° C. and 100° C. be taken as 100 degrees on the absolute scale, then the absolute zero of temperature is almost exactly − 273° C. Temperature readings on the absolute scale are therefore very nearly identical with those on the hydrogen thermometer, although the principles on

* Lord Kelvin's *Mathematical and Physical Papers*, vol. i, p. 104.

which the two scales are formed have no connection with each other. The amount by which the readings of the hydrogen thermometer differ from those of the absolute scale may be deduced from Lord Kelvin's experiments.

The absolute thermodynamic scale may be represented graphically as in fig. 187.

Let ABC be an isothermal line for any temperature θ, the point A corresponding to the initial state of the working substance, and the points B and C to its condition after the addition to it of quantities of heat equal to H and 2H respectively. Also let LMN be the isothermal for $\theta = 0$.

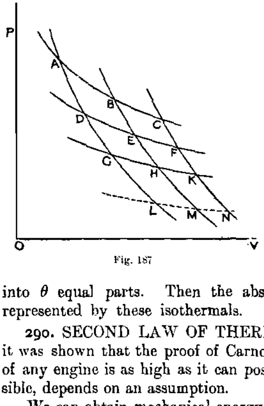

Fig. 187

Through the points A, B, and C let the adiabatics AL, BM, CN be drawn. Then the areas ALMB, BMNC are equal to one another, as each represents the work done by a perfect engine, which takes in heat H at θ and, having its refrigerator at the absolute zero of temperature, transforms all the heat it receives into work. Between ABC and LMN let a number (equal to $\theta - 1$) of isothermals be drawn, dividing the areas ALMB, BMNC into θ equal parts. Then the absolute scale of temperature is represented by these isothermals.

290. SECOND LAW OF THERMODYNAMICS.—In Art. 286 it was shown that the proof of Carnot's principle that the efficiency of any engine is as high as it can possibly be if the engine is reversible, depends on an assumption.

We can obtain mechanical energy by allowing heat to pass from a hot body A to a colder body B, but if the temperature of A falls to that of B the transfer of heat and the performance of mechanical work cease; and so long as we limit our attention to those two bodies and do not employ mechanical work upon them, no more work can be obtained.

The body A still contains a store of energy, but our only opportunity of utilizing any of this is while it is passing in the form of heat from A to some colder body.

This fact is embodied in the second law of thermodynamics, which has been thus stated by Clausius:—

"*It is impossible for a self-acting machine unassisted by any external agency to convey heat from a colder to a warmer body.*"

The second law of thermodynamics is an independent axiom separate from and not deduced from the first law of thermodynamics or from any principle of dynamics. It is based on experimental evidence only, and in its turn serves as the basis of the theory of heat engines.

The main evidence of its truth is that deductions made from the law agree with experience. The transformation of non-mechanical energy, i.e. heat, into mechanical energy is the summation of a large number of small quantities of energy and the application of this energy to the movement of a larger body. And the practicability of this process is limited. We cannot take, say, a million molecules in rapid motion and cause them to use up the whole of their energy in communicating mechanical motion to some larger body. If the molecules could be dealt with individually this might be done, and the second law of thermodynamics would not hold good, but experimentally we can only deal with masses of molecules, and the law expresses this limitation of our powers.

It must be remembered that this law applies only to engines working in reversible cycles and to reversible cyclic processes. It is possible to transfer heat from a colder to a warmer body; but when it is not possible to repeat the changes of the working substance precisely in the reverse order, and by that means restore it to its original state, the process is an irreversible one, to which the second law of thermodynamics is not applicable. Thus water in evaporating from a vessel cools it below the temperature of surrounding objects, and work could be obtained from the vapour that is evolved; but this is no violation of the law, because in the operation as far as described there is no cycle of operations.

So, too, compressed air in escaping from a cylinder expands and does work, and the temperature of the cylinder falls. But the air not merely cools, it has changed its volume also; and if it be caused to return to the same volume and condition, the whole cyclic process will be found to be in accordance with the law.

Hirn propounded the following operation as a difficulty in accepting the law.

He imagined two exactly similar cylinders A and B (fig. 188) impervious to heat and connected at the bottom by a small pipe.

In each cylinder works an air-tight frictionless piston, and by means of a toothed wheel one piston can be raised and the other simultaneously lowered to an equal extent. At the start the cylinder A is filled with air at 0° C. and B is empty. The pipe C is kept at 100° C. throughout the operation. Let now the wheel be revolved, so that some air passes from A to B. This air is raised to 100° C. in its passage through C, and owing to this rise in temperature its pressure increases. This pressure transmitted through C raises the pressure of the air in A, and the compression raises the temperature. As the process continues the pressure continues to rise in both cylinders, and heat is continuously developed thereby, until when all the gas has passed from A to B the temperature of the gas has been raised to a value greater than 100° C. The gas occupies the same volume as at first; no mechanical work has been done on it, and its temperature has been raised above that of its surroundings.

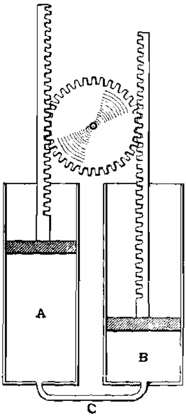

Fig. 188

But it must be noted that while the gas was passing through the pipe, heat was passing from a higher to a lower temperature. So that there were really two processes proceeding—one that of a direct engine, which took in heat at 100° C. and gave it out at a lower temperature; the other that of a reversed engine, which took in heat at a lower and gave it out at a higher temperature. The total quantity of heat transferred in the two processes is the same. Heat did really pass from a cold body to a hot one, but only by the introduction of a direct heat engine. The process was not a simple cycle.

In a cyclic operation the body is brought back to its original state, and there is no change in its *intrinsic energy*. The intrinsic energy of a body is the total work that it could do in the process of parting with all its heat. It cannot be measured, because there is no practical means of depriving a body of all its heat. Changes in

its amount are measured by the amount of energy that enters or leaves during any operation, as expressed by the equation $dE = dH - dW$. In a perfect gas the intrinsic energy depends only on the temperature.

291. **Refrigerating Machines.**—In a class of machines used for purposes of refrigeration, heat is taken in at a lower temperature and given out at a higher temperature.

Fig. 189 shows an arrangement for cooling a chamber by this means. A and B represent the two cylinders of the engine which, through pipes containing valves, are in communication with the chamber C. Other pipes containing valves connect the cylinders

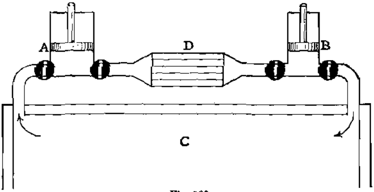

Fig. 189

with a cooler D, which consists of a chamber through which run a number of tubes. Cold water is kept running through these tubes. When the piston of A rises, air passes from the chamber into this cylinder, and when the piston falls this air is heated and compressed. In this condition it passes into the cooler D. Leaving the cooler it passes into the cylinder B, where it does work in helping to raise the piston. By this process it is cooled, and then by the descent of the piston is driven into the chamber C. In ordinary practice the temperature of the air after compression is about 150° C., is reduced to about 15° or 20° C. in the cooler, and to about − 40° C. by the expansion.

292. DISSIPATION OF ENERGY.—It has been shown that when a quantity of heat H is taken in at a higher temperature by a *perfect* engine, an amount of work W is done and a quantity of heat h is given out at a lower temperature. The heat taken in can never all be converted into work by any engine. The heat h which is thus rejected is dissipated or degraded; it has ceased to be available for working purposes, or is at any rate less available. The availability

of heat depends on its temperature, and since bodies at a higher temperature are always tending to fall to a lower temperature, and since every form of energy can be transformed into heat, and such transformations are always going on, it follows that there is a tendency for all forms of energy to take the form of diffused heat of low temperature.

293. ENTROPY.—The conception of entropy which was touched on in Art. 271 is much used in working certain problems connected with the steam engine. When heat enters or leaves a body at a definite fixed temperature, there is a change in its entropy, the relation being

$$\text{Change of entropy} = \frac{\text{Quantity of heat passing}}{\text{Absolute temperature of the body}}.$$

Thus, suppose we have unit mass of water at 100° C., and we convert it into steam at 100° C., then its entropy, taking Regnault's value for L, has increased by $\frac{536 \cdot 5}{373} = 1 \cdot 4383$ unit. It has been proposed to call this unit a **rank** (after Rankine). Entropy is usually denoted by the symbol ϕ, and the above equation of definition may be written

$$\phi = \frac{H}{\theta}.$$

The entropy of a substance depends on its thermal state, and is always the same when the substance is in the same state. The actual amount of the entropy of a substance cannot be stated, but only the excess or defect from the amount which it possesses when in a standard state. For water the state is that which exists at *0° C. and 760 mm. pressure. That is taken as the zero of entropy.*

In this section all the temperatures are measured from absolute zero (– 273° C.). Suppose we have unit mass of water at 273° A., and it is heated to 274° A. There has been added to it one unit of heat, and this has been done at temperatures the mean of which is 273·5° A. Dividing the unit of heat by 273·5, the quotient is ·00365. Approximately ·00365 unit of entropy has been added to the water, and if we suppose that at 273° A. the water possessed no entropy (which is a convenient practical convention), then the entropy of unit mass of water at 274° A. is ·00365 unit. It will be observed that this result is not quite accurate, for the heat was added and the temperature was raised gradually, the process really consisting of an infinite number of very small steps.

Let a very small quantity of heat dH be added at temperature θ, and let the rise of temperature be $d\theta$, then if $d\phi$ is the increase of entropy

$$d\phi = \frac{dH}{\theta}.$$

If we take the specific heat of water as unity, then dH is numerically equal to $d\theta$, and

$$d\phi = \frac{d\theta}{\theta}.$$

Integrating this equation we have

$$\phi + c = \log_e \theta$$

where c is a constant depending on the origin.

Starting from 273° A. and dealing only with excesses of temperature above this, and writing ϕ_θ for the value of the entropy at any temperature θ,

$$\phi_\theta = \int_{273}^{\theta} \frac{d\theta}{\theta} = \log_e \theta - \log_e 273$$
$$= 2{\cdot}3026\,(\log_{10}\theta - \log_{10} 273).$$

At 274° A. $\quad \phi = \int_{273}^{274} \frac{d\theta}{\theta} = \log_e 274 - \log_e 273$
$= 2{\cdot}3026\,(\log_{10} 274 - \log_{10} 273)$
$= 2{\cdot}3026\,(2{\cdot}43775 - 2{\cdot}43616)$
$= {\cdot}00366.$

At 373° A. $\quad \phi = 2{\cdot}3026\,(\log 373 - \log 273)$
$= 2{\cdot}3026\,(2{\cdot}57171 - 2{\cdot}43616)$
$= {\cdot}3121.$

Proceeding in this way we obtain the table of values of ϕ for water at various temperatures set out below:—

Temperature.	Latent Heat of Steam.	Entropy.	
		Water ϕ.	Steam ϕ_1.
0° C.	606·5	0	2·221
20°	592·6	·0707	2·093
40°	587·6	·1366	2·014
60°	564·7	·1984	1·894
80°	550·6	·2567	1·816
100°	536·5	·3121	1·75
120°	522·3	·3645	1·693
140°	508·0	·4155	1·646
160°	493·5	·461	1·602
180°	479	·506	1·566
200°	464·3	·549	1·531

Steam.—To convert unit mass of water into steam at any temperature θ we must add to it the latent heat at θ. Therefore the entropy (ϕ_1) of steam at any temperature is obtained by adding to the entropy of water (ϕ) at that temperature the quotient $L_\theta \div \theta$.

$$\phi_1 = \phi + \frac{L}{\theta};$$

$$\text{thus at } 373^\circ \text{ A., } \phi_1 = \cdot 31212 + 1\cdot 4383 = 1\cdot 7504.$$

The latent heat of steam at any temperature is known from Regnault's formula (Art. 114). Hence the entropy of water at any temperature having been calculated by the method shown above, the entropy of steam at any temperature becomes known. Some values are given in the table above.

In the diagram of fig. 190, called a temperature-entropy or $\theta\phi$ diagram, the values of the temperature and entropy of water and steam given in the above table have been plotted, the temperatures being taken as ordinates and the entropy as abscissæ. On this diagram the horizontal lines are the isothermals, and the vertical lines, which are lines of equal entropy or isentropics, are adiabatics, while quantities of heat ($\theta \times \phi$), i.e. work, are represented by rectangular areas. Owing to the analogy between the statements *Heat* = *Temperature* × *Entropy*, and *Work* = *Weight* × *Height* (Art. 207), Zeuner called temperature thermic height and entropy thermic weight.

The $\theta\phi$ diagram is especially useful in solving problems relating to water and steam when both are existing together.

Thus, suppose we have unit mass of steam at 120° C. corresponding to the point Q on the diagram, and the substance falls in temperature to 100° C. under adiabatic conditions. Draw the vertical line QG on to the entropy line of 100° C. Then the fact that the point G is between C and D indicates that part of the steam is converted into water, and further

$$\frac{\text{the mass of water}}{\text{the mass of steam}} = \frac{\text{DG}}{\text{CG}}.$$

Again, suppose water be raised to 120° C. without evaporation, then its entropy will be represented by the line FP (·36 unit); when the substance is all converted into steam, by the line FQ (1·69 unit). When six-tenths is water and four-tenths steam the entropy is represented by the line FS (·9 unit), the point S being marked so that PS = $\frac{4}{10}$ PQ. The heat absorbed during this process in

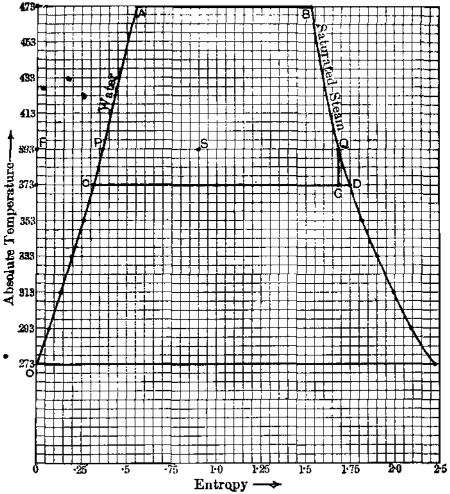

Fig. 190

passing from the condition marked by the point O to that indicated by the point S is represented by the product OF × PS.

294. Specific Heat of Saturated Steam.—Suppose we have unit mass of water at 99° C. (372° absolute).

(*a*) Let its temperature be raised from 99° C. to 101° C. without evaporation. The heat absorbed = 2 units.

(*b*) Let the water be evaporated at 101° C. The heat absorbed is the latent heat at 101° C., which from Regnault's formula (Art. 114) = 606·5 − (·695 × 101) = 536·305 units.

(*c*) Let the temperature of the steam be lowered to 99° C. without condensation, then the heat given out = 2S units where S is the specific heat required.

(*d*) Let the steam be condensed into water at 99° C. Then the heat given out $= 606{\cdot}5 - ({\cdot}695 \times 99) = 537{\cdot}695$ units.

Heat taken in =

$$\begin{aligned} H &= 2 + 536{\cdot}305 - 2S - 537{\cdot}695 \text{ units} \\ &= -2S + {\cdot}61. \end{aligned}$$

And the work done is shown by the $\theta\phi$ diagram to be equal to the difference between the entropy of water and steam at 100° C. (the mean temperature) multiplied by the difference of temperature, which is two degrees.

$$\begin{aligned} W &= 2 \times 1{\cdot}438. \\ \text{But } H &= W \\ \therefore -2S + {\cdot}61 &= 2{\cdot}878 \\ \text{and } S &= -1{\cdot}133. \end{aligned}$$

295. Generally for any substance which changes its state from liquid to vapour—

if S_1 = the specific heat of the liquid,

S_2 = that of the vapour at the same temperature,

θ and $\theta + d\theta$ = lower and higher temperatures respectively,

L = the latent heat of the vapour at temperature θ,

and $\dfrac{dL}{d\theta}$ = rate of change of the latent heat with temperature;

we have in the successive operations detailed above—

(*a*) Heat taken in $= S_1 d\theta$

(*b*) Heat taken in $= L + \dfrac{dL}{d\theta}\, d\theta$

(*c*) Heat given out $= S_2 d\theta$

(*d*) Heat given out = L

$$\therefore H = (S_1 - S_2)d\theta + \frac{dL}{d\theta}\, d\theta$$

$$\text{and } W = \frac{L}{\theta}\, d\theta.$$

Equating the values of H and W and dividing by $d\theta$ we have—

$$S_1 - S_2 + \frac{dL}{d\theta} = \frac{L}{\theta}.$$

The quantity $\dfrac{dL}{d\theta}$ is positive for some substances and negative for others (e.g. saturated steam).

296. Entropy of a Perfect Gas.—In Art. 239 the equation between heat and work when a small quantity of heat was communicated to a gas, was found to be—

$$dH = C_v d\theta + P dV.$$

$$\text{Now since } P = R\frac{\theta}{V}$$

$$\therefore dH = C_v \frac{d\theta}{\theta} + R\theta\frac{dV}{V}$$

$$\therefore \frac{dH}{\theta} = C_v \frac{d\theta}{\theta} + R\frac{dV}{V}.$$

Integrating between the limits θ_1 and θ_2—

$$\int_{\theta_2}^{\theta_1} \frac{dH}{\theta} = \phi_1 - \phi_2 = C_v \log_e \frac{\theta_1}{\theta_2} + R \log_e \frac{V_1}{V_2}$$

or with ordinary logarithms.

$$\therefore \phi_1 - \phi_2 = 2{\cdot}3026 \left\{ C_v \log \frac{\theta_1}{\theta_2} + R \log \frac{V_1}{V_2} \right\}$$

Taking for illustration the change of entropy along the line BC (fig. 186) in Art. 288 we have—

$$\phi_1 - \phi_2 = 2{\cdot}3026 \left\{ {\cdot}1685 \log 1 + {\cdot}069 \log \frac{5{\cdot}793}{8{\cdot}689} \right\} = {\cdot}028.$$

The result may also be calculated from the quantities given in Art. 288; thus—

$$\phi = \frac{W}{J} \div \theta = \frac{14534}{1390} \times \frac{1}{373} = {\cdot}028.$$

Taking the corresponding quantities for the change along the line DA we have—

$$\phi = \frac{10637{\cdot}5}{1390} \times \frac{1}{273} = {\cdot}028.$$

297. EXAMPLES.

1. The temperatures of the boiler and condenser of a steam engine are 150° C. and 50° C. respectively. What proportion of the heat supplied will be utilized if the engine is a perfect engine?

$$\text{Efficiency} = \frac{\theta_2 - \theta_1}{\theta_2}$$

$$= \frac{100}{273 + 150} = \frac{100}{423}$$

$$= {\cdot}236 = 23{\cdot}6 \text{ per cent.}$$

2. If a perfect engine, whose efficiency is $\frac{1}{9}$, gives out heat at 40° C., what is the temperature of the source?

$$\frac{W}{H} = \frac{\theta_2 - \theta_1}{\theta_2}$$

$$\frac{1}{9} = \frac{\theta_2 - 313}{\theta_2}$$

$$\theta_2 = 9\theta_2 - 2817$$

$$\therefore 8\theta_2 = 2817$$

$$\theta_2 = 352 \text{ nearly.}$$

The temperature is 79° C. nearly.

3. The resistance to the motion of a train is equal to the weight of 15 cwt. *If 20 lb. of coal are consumed for every mile run by the train, and if the heat* produced by the combustion of 1 lb. of coal be capable of converting 15 lb. of water at 100° C. into steam at 100° C.; compare the efficiency of the engine with that of a reversible engine, working between 150° C. and 114° C.

Suppose the train to run 1 mile, then

(i) *Work done by engine*

$$= (15 \times 112) \times 1760 \times 3 \text{ foot-pounds.}$$

(ii) Energy supplied to engine

$$= 20 \times 15 \times 536 \text{ units of heat}$$

$$= 20 \times 15 \times 536 \times 1390 \text{ foot-pounds.}$$

$$\therefore \text{Efficiency} = \frac{15 \times 112 \times 176 \times 3}{15 \times 536 \times 139 \times 20} = \frac{14 \times 44 \times 3}{67 \times 139 \times 5} = \frac{1848}{46565}$$

$$= 3{\cdot}97 \text{ per cent.}$$

The efficiency of the reversible engine is $\frac{\theta_2 - \theta_1}{\theta_2} = \frac{36}{423} = 8{\cdot}51$ per cent.

The required ratio is therefore $\frac{397}{851}$.

QUESTIONS AND EXERCISES

1. What is meant by the dissipation of energy, and how is the doctrine of dissipation of energy connected with the second law of thermodynamics?
2. What do you understand by a reversible heat engine, and what is meant by the efficiency of a machine? How would you show that the efficiency of all reversible heat engines, working between the same limits of temperature, is the same?
3. What is the theoretical efficiency of a steam engine whose boiler is at 150° C. and condenser at 40° C.?
4. If steam were admitted into a cylinder at a pressure of 15 lb. and a temperature 212° F., and were expanded to a temperature of 100° F., what is the greatest amount of work which could be done if the engine were perfect?
5. An air engine takes in heat at 300° F., and gives out heat at 50° F. Find theoretically the amount of work the engine could do if certain conditions were capable of being realized. State these conditions, and draw the indicator diagram of the engine.

6. Find the approximate value of the specific heat of saturated steam at 200° C. if the rate of increase of the total heat be taken as ·3 per degree Centigrade.
7. Find the efficiency of an air engine using 1 lb. of coal per horse-power hour, and compare it with that of a perfect reversible engine, assuming that the heater is at 1000° C. and the refrigerator at 0° C., and that the thermal value of the coal is 8000 calories per grm.

CHAPTER XXVII

SOME APPLICATIONS OF CARNOT'S PRINCIPLE

298. *INFLUENCE OF PRESSURE UPON TEMPERATURE OF FUSION.*

Professor James Thomson first pointed out that it followed from the above principles that the melting-points of all substances that expand on solidification are lowered by an increase and raised by a decrease of pressure; while for substances that expand on liquefaction the opposite is the case. His argument was of the following nature.

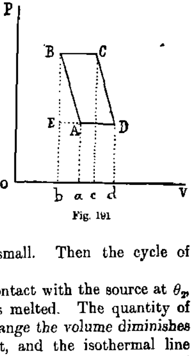

Fig. 191

During such changes of state the substances are working as perfect engines. Suppose unit mass of a solid at its temperature of liquefaction (θ_2) and under pressure P to be contained within the working cylinder of Carnot's perfect engine, and suppose the solid to be one that expands on solidification. Let the temperature of the source be θ_2 and that of the refrigerator θ_1, the difference $\theta_2 - \theta_1$ being very small. Then the cycle of operations may be thus conducted:—

(i) The solid substance is placed in contact with the source at θ_2, and heat is taken in until the whole is melted. The quantity of heat absorbed is L units. During the change the volume diminishes while the temperature remains constant, and the isothermal line traced out on the diagram is CB (fig. 191). Let the change of volume indicated by *cb* be *u*.

(ii) The cylinder is then placed on the non-conducting stand, and the condition of the substance changes without loss or gain of heat

until the temperature has fallen to θ_1. The adiabatic line BA has been traced out on the diagram.

(iii) Let the cylinder be then placed in contact with the refrigerator at the temperature θ_1. The temperature remains constant, the liquid solidifies, and the volume increases. The line traced out in the diagram is the isothermal AD.

(iv) Lastly, let the cylinder be placed on the non-conducting stand and the substance brought back to its original condition without loss or gain of heat. The line traced out on the diagram is the adiabatic DC.

Since the substance is warmer in the first stage than in the third, its pressure is greater during that stage, and work is therefore on the whole done upon it. If the substance contract on solidification, the contrary is the case. The quantity of this work is represented by the area ABCD $=$ BC $\times$ BE $= u \times dP$; and the heat taken from the source is L.

$$\text{But } \frac{\text{External work}}{\text{Heat taken from source}} = \frac{\theta_2 - \theta_1}{\theta_2}$$

$$\therefore \frac{u \times dP}{L} = \frac{\theta_2 - \theta_1}{\theta_2}.$$

$$\text{Writing } \theta_2 - \theta_1 = d\theta;\ L \times d\theta = u \times dP \times \theta_2$$

$$\text{or } L = u \times \theta_2 \times \frac{dP}{d\theta}.$$

Where L is the latent heat of fusion of unit mass in dynamical units, u is the difference in volume of unit mass in the solid and liquid states, θ_2 is the absolute temperature of the source, dP is the change of pressure measured in absolute units, correspondiug to the change of temperature $d\theta$.

If u is positive then $\frac{dP}{d\theta}$ is positive; if u is negative then $\frac{dP}{d\theta}$ is negative.

299. EXAMPLES.

(i) **Water.** For 1 grm. of ice at 0° C.,

$$L = 79{\cdot}25 \times 42 \times 10^6 \text{ ergs}$$
$$u = {\cdot}089 \text{ c.cm.}$$
$$\text{and } \theta_2 = 273.$$

The connection between a change of pressure dP and $d\theta$ the corresponding change of temperature is thus—

$$79{\cdot}25 \times 42 \times 10^6 \times d\theta = {\cdot}089 \times 273 \times dP$$
$$\therefore d\theta = dP \times {\cdot}73(10)^{-8}.$$

If the change of pressure be one atmosphere

$$dP = 1033 \times 981 \text{ dynes per sq. cm.}$$
$$= 1{\cdot}014 \times 10^6 \text{ dynes} \quad ,,$$
$$\text{Whence } d\theta = {\cdot}0074.$$

The difference between the temperature of water when freezing *in vacuo* and when freezing under atmospheric pressure is ·0074° C.

(ii) Calculate the effect of an atmosphere of pressure on the melting-point of a substance which contracts on solidifying by one-sixth of its volume in the liquid state, whose latent heat is 40 units, whose ordinary freezing-point is 27° C., and whose specific gravity when liquid at this temperature is 1·2.

Take 1 grm. of the liquid ; then its volume $= \frac{1}{1{\cdot}2} = {\cdot}833$ c.cm. The *reduction of volume on solidification is* $\frac{1}{6}$ *of* ·833 = ·139 c.cm. = *u*.

The change of pressure $dP = 1{\cdot}014 \times 10^6$ dynes per sq. cm.

Hence since $\qquad L \times d\theta = \theta_2 \times u \times dP$

$$\therefore\ 40 \times 41{\cdot}6 \times 10^6 \times d\theta = (273 + 27) \times {\cdot}139 \times 1{\cdot}014 \times 10^6$$
$$d\theta = \frac{1}{40}\left\{300 \times {\cdot}139 \times \frac{1{\cdot}014}{41{\cdot}6}\right\}$$
$$= \frac{1}{40}\left\{41{\cdot}7 \times \frac{1{\cdot}014}{41{\cdot}6}\right\}$$
$$= {\cdot}0253^\circ \text{ C.}$$

In such examples as the above, when we are dealing with substances other than water, the density is involved. This is owing to the fact that unit mass is dealt with, and it is necessary to know the change of volume undergone by that unit mass. If the heat rendered latent be known in the form of so many units of heat per unit volume, the necessity for knowing the density is obviated.

(iii) Suppose a substance whose latent heat is 50 calories per unit volume melts at 127° C. *in vacuo*, and contracts one-tenth of its bulk in so doing; at what temperature will it melt under a pressure of 100 atmospheres?

Take one unit volume. Then for the energy absorbed when it melts we have

$$H = 50 \times 4{\cdot}20 \times 10^6 = 2100 \times 10^6 \text{ ergs.}$$

And the work done against the external pressure of 100 atmospheres $= -W$

$$= -\tfrac{1}{10} \times 1{\cdot}014 \times 10^6 \times 100 = 10{\cdot}14 \times 10^6 \text{ ergs;}$$
$$\text{but } \frac{W}{H} = \frac{\theta_2 - \theta_1}{\theta_2} = \frac{d\theta}{\theta_2}$$
$$\therefore\ d\theta = -\frac{10{\cdot}14}{2100} \times 400$$
$$= -1{\cdot}93^\circ \text{ C.}$$

The melting-point is therefore 125·07° C.

300. EFFECT OF PRESSURE ON TEMPERATURE OF VAPORIZATION.—Similar reasoning to that employed above applies to the change from the liquid to the gaseous states, and for this change also we may write

$$L = u \times \theta_2 \times \frac{dP}{d\theta}.$$

An interesting application of this is to obtain the value of u for steam.

The increase of pressure dP corresponding to a rise $d\theta$ of 1° C. in temperature from 99·5° C. to 100·5° C. is given in Regnault's tables as 2·721 cm. of mercury,

$$\therefore \frac{dP}{d\theta} = 2{\cdot}721 \times 13{\cdot}596 \times 981$$
$$= 36275.$$
$$\text{Also } L = 540{\cdot}2 \times 41{\cdot}83 \times 10^6$$
$$= 22596 \times 10^6$$
$$\therefore u = \frac{22596 \times 10^6}{373 \times 36275}$$
$$= 1670.$$

The above equation also holds for sublimation. The latent heat of sublimation is the quantity of heat absorbed in the vaporization of unit mass of the solid. This quantity can be calculated from the change of vapour pressure with temperature, and the specific volumes (volumes of unit mass) of the substance as vapour and solid at any given temperature.

301. CRITICAL TEMPERATURE.—The expression for the latent heat is written

$$L = u \times \theta_2 \times \frac{dP}{d\theta}.$$

As the temperature rises the factor $\frac{\theta_2 dP}{d\theta}$ increases, while the factor u diminishes. When the factor u becomes equal to zero, vaporization takes place without change of volume, and L becomes also zero. The value of θ_2 when this occurs is the *critical temperature*, the existence of which is thus shown by theory.

The Triple Point.—At this temperature the solid and liquid states are in equilibrium, and the vapour pressure of the solid must be equal to that of the liquid. For if one pressure were greater than the other, an engine could utilize this difference of pressure, and work could be continuously obtained from two bodies which are always at the same temperature.

302. ADIABATIC COMPRESSION. — The change of temperature that takes place in a substance when it is adiabatically compressed may also be determined by this method. Take unit volume of the substance in the condition as to pressure and volume represented by the point A (*fig.* 191).

(i) Let the substance be adiabatically compressed until its pressure and volume correspond to the point B. During this operation the temperature rises from θ_1 to θ_2, and the pressure from P_1 to P_2.

(ii) *Let the substance expand under constant pressure until its* condition corresponds to the point C. During this operation a quantity of heat H is taken in equal to the product of Q the thermal capacity of unit volume at constant pressure measured in dynamical units, and $d\theta$ the change of temperature,

$$\text{then } H = Q\,d\theta.$$

Also if y be the coefficient of expansion at constant pressure, then BC the increase of volume is equal to $y \times d\theta$.

(iii) The substance expands adiabatically, tracing out the path CD, and returning to its original pressure.

(iv) *The substance contracts at constant pressure, tracing out* the path DA and returning to its original state.

$$\text{The work done} = \text{area ABCD} = \text{BC} \times \text{BE}$$

$$\therefore W = y \times d\theta\,(P_2 - P_1).$$

The heat taken in $= Q \times d\theta$; and writing dP for $P_2 - P_1$,

$$\text{Efficiency} = \frac{W}{H} = \frac{y \times dP \times d\theta}{Q \times d\theta} = \frac{y \times dP}{Q}.$$

But the efficiency is also equal to $\dfrac{d\theta}{\theta_2}$

$$\therefore d\theta = \frac{\theta_2 \times y \times dP}{Q}$$

$$or\ Q = \theta_2 \times y \times \frac{dP}{d\theta}.$$

But Q the thermal capacity of unit volume at constant pressure is equal to the specific heat at constant pressure K_p multiplied by the absolute density ρ of the substance,

$$\therefore d\theta = \frac{\theta_2 \times y \times dP}{K_p \times \rho}.$$

Example.—Thus we may find the rise in temperature produced in water at 17° by an additional pressure of one million dynes per square centimetre—

y the coefficient of expansion of water at 17° C. $= \cdot 00018$, $K_p = 42 \times 10^6$, and $\rho = 1$,

$$\text{whence } \theta = \frac{\cdot 00018 \times (1 \times 10^6) \times 290}{42 \times 10^6}$$

$$= \cdot 00124°.$$

303. SURFACE TENSION.—Lord Kelvin showed that since the surface tension of a liquid film diminishes as the temperature increases, *stretching* such a film must cool it; i.e. if L be the

number of units of heat absorbed per unit area to keep the temperature constant when the film is drawn out, then L must be a positive quantity.

Take a film whose initial area is a, surface tension f, and temperature θ, its condition being represented by the point A on the diagram (fig. 192).

(i) Let the film be extended isothermally until its area is b, its state being thus represented by the point B on the diagram. Then the heat absorbed from the source is $L(b - a)$.

(ii) Let the film contract adiabatically until its area is c and its state represented on the diagram by the point C. During this process the film does work, and its temperature alters by an amount $d\theta$. Suppose the surface tension to increase by an amount df.

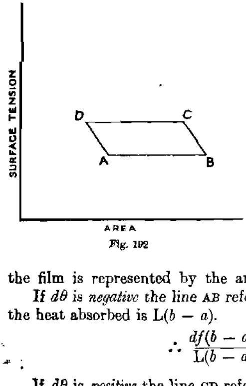

Fig. 192

(iii) Let the film contract isothermally until its state corresponds to the point D on the diagram, which is on the adiabatic passing through A.

(iv) Let the film be extended adiabatically until its condition is represented by the point A on the diagram, and the cycle is completed.

Then the net work done by the film is represented by the area ABCD $= df\,(b - a)$.

If $d\theta$ is *negative* the line AB refers to the higher temperature, and the heat absorbed is $L(b - a)$.

$$\therefore \frac{df(b-a)}{L(b-a)} = \frac{-d\theta}{\theta}.$$

If $d\theta$ is *positive* the line CD refers to the higher temperature, and the heat absorbed is $- L(b - a)$.

$$\therefore \frac{df(b-a)}{-L(b-a)} = \frac{d\theta}{T}$$

So that in either case

$$\frac{df}{L} = -\frac{d\theta}{\theta}$$

$$\text{or } \frac{df}{d\theta} = -\frac{L}{\theta}.$$

But experiment shows that df and $d\theta$ are of opposite signs, so that $\frac{df}{d\theta}$ is always negative, therefore L is a positive quantity, i.e. heat is absorbed when a film is drawn out.

304. FULL RADIATION IN AN ENCLOSURE.—One of the deductions made by Clerk-Maxwell from his electromagnetic theory of light was that light exerts a pressure in the direction of its line of propagation. With the light falling normally on a surface he calculated the pressure per square centimetre (P) to be numerically equal to the amount of energy contained in 1 c.cm. of the medium in the region of the point. This quantity (E) is termed the energy density of the medium.

It may be shown that inside a hollow sphere which constitutes a fully radiating enclosure, the pressure P on unit area at its centre, and the energy density E within the sphere, are connected by the equation

$$E = 3P.$$

Imagine such a sphere at a temperature θ, and regard the interior radiation as the working substance of a perfect heat engine, changes of volume taking place under and against the pressure of the radiation, and no other forces entering into the arrangement.

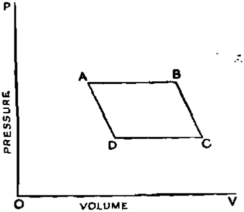

Fig. 193

Then the cycle of operations is as follows:—

(i) The temperature being θ, the pressure P, and the volume V, the sphere whose inner surface is fully radiating is allowed to increase in volume isothermally by an amount dV under the pressure P, the work done being P × dV. Also energy must be given out by the source to fill the space dV, and this amount is E × dV. Thus the total energy given out by the source is

$$(E + P)dV = dH$$

The line AB is traced out on the diagram (fig. 193).

(ii) During the second operation the inside surface of the sphere is totally reflecting and non-conducting, and the volume is allowed to

increase adiabatically under the pressure of the radiation. During this operation the pressure gradually falls to P − dP, the energy density to E − dE, and the temperature to $\theta - d\theta$. The energy density diminishes during the operation, owing both to the increase in volume and to the work done by the pressure in forcing out the boundary.

The line BC is traced out on the diagram.

(iii) The inner surface of the sphere is now made fully radiating as in the first operation. The temperature remaining at $\theta - d\theta$, the volume decreases isothermally under the pressure P − dP until the point D is reached on the diagram, this point being on the adiabatic passing through A.

(iv) The surface being again made fully reflecting, the volume is diminished adiabatically to V, the temperature and pressure rising to their original values.

The line DA *is traced out on the diagram and the* Carnot *cycle is* completed.

The work done is shown by the diagram to be $dP \times dV$.

The energy taken in from the source was $(E + P)dV$.

Therefore

$$\frac{dP \times dV}{(E+P)dV} = \frac{d\theta}{\theta}$$

or writing $\frac{E}{3}$ for P and $\frac{dE}{3}$ for dP

$$\frac{dE}{E} = 4\frac{d\theta}{\theta},$$

and integrating

$$\log E + \text{a constant} = 4 \log \theta = \log \theta^4$$
$$\therefore E = a\theta^4$$

i.e. *the energy density within the enclosure is proportional to the fourth power of the temperature*—the Boltzmann-Stefan law (Art. 183).

QUESTIONS AND EXERCISES

1. Ice melts at 32° F. and wax at 140° F. A mass of ice at 31° and a mass of wax at 139° are separately compressed by suitable means. Could either of them by a sufficient increase of the pressure be melted? Give reasons for your answer.

2. State the second law of thermodynamics, and apply it to the determination of the effect of pressure on the melting-point of a solid.

3. Calculate the rise in temperature of boiling water if the pressure increase from an atmosphere to 1·1 atmosphere.
4. From the data given calculate the change in the melting-point due to the change of pressure placed in the last column of the following table:—

Substance.	Melting-point.	Volume at 0° C.	Volume at Melting-point.		Density of Solid.	Latent Heat.	Change of Pressure.
			Solid.	Liquid			
Phosphorus ...	44° C.	1	1·017	1·052	1·83	5·2	10 atmos.
Sulphur ...	115°	1	1·096	1·150	2·0	9·4	20 „
Wax	64°	1	1·161	1·166	·96	97	50 „

MISCELLANEOUS EXAMPLES AND EXERCISES

1. Specific Heat.—The method indicated in Art. 77 is sometimes employed for determining high temperatures.

A ball of platinum, whose mass is 200 grm., is removed from a furnace, and immersed in 150 grm. of water at 0° C. If we suppose the water to gain all the heat which the platinum loses, and if the temperature of the water rises to 30°, determine the temperature of the furnace.

The specific heat of platinum is 0·031.

Let x° C. be the heat of the furnace; then

(1) Heat given out by the ball in cooling from x° to 30°,

$$= 200 \times (x - 30) \times \cdot 031.$$

(2) Heat absorbed by the water $= 150 \times 30$;

$$\therefore 6{\cdot}2 \times (x - 30) = 4500.$$
$$\therefore 6{\cdot}2\, x = 4686.$$
$$x = 755{\cdot}8° \text{ C.}$$

2. Find the rate at which ice on a pond will increase in thickness when the air in contact with its upper surface is maintained at $-\tau$° C.

In order that freezing may take place the latent heat of liquefaction must be conducted away through the ice. Let the thickness of the ice at any given moment be l, then for the next small period of time dt, during which a thickness dl freezes, the heat emitted by unit area is

$$\text{H} = dl \times 1 \times \cdot 917 \times 80 = 73{\cdot}36\, dl.$$

$$\therefore 73{\cdot}36\, dl = k \times 1 \times \tau \times \frac{1}{l} \times dt.$$

$$\therefore \frac{k\tau}{73{\cdot}36} = l\frac{dl}{dt} \quad \ldots\ldots \quad (1)$$

Thus given $k = \cdot 0022$, $\tau = 12$, and $l = 5$

$$\frac{dl}{dt} = \frac{\cdot 0022 \times 12}{73{\cdot}36 \times 5} = \cdot 000072.$$

Equation (1) may be written

$$\frac{k\tau}{73{\cdot}36} \cdot dt = l\, dl$$

the integration of which gives

$$\frac{k\tau}{73 \cdot 36} \cdot t = \frac{l^2}{2} \quad \text{.......... (2)}$$

$$\text{or} \quad l^2 = t \frac{k\tau}{36 \cdot 68}.$$

The form of the equation shows that the curve giving the progress of the thickness with time is a parabola. But the actual conditions are not those of the steady flow of heat contemplated in Art. 140, and the result is only approximate.

With this proviso, taking k and τ with the same values as above, then

$$1389\, l^2 = t$$

and by giving l the successive values 1, 2, 3 cm., we obtain for t values about 23, 92, and 207 min. as the times of formation of those thicknesses.

3. What average excess in temperature in a chimney 136 ft. high would produce a pull measured by 1 in. on the water gauge?

Suppose the hot gas in the chimney to be at τ° C. and the air outside at 0° C. If the sectional area of the chimney be taken as 1 sq. ft., then the weight of the counterbalancing column of air outside is 136 × ·0807 = 10·97 lb., and this is equal to the weight of 136 c. ft. of air at τ° C. + the weight of $\frac{1}{12}$ c. ft. of water, which is 5·2 lb.

$$\therefore (10 \cdot 97 - 5 \cdot 2)\left(1 + \frac{\tau}{273}\right) = 10 \cdot 97$$

$$\therefore \tau = 246° \text{ C.}$$

4. *If a plate of iron 1 ft. square and 1 in. thick transmit 7·5 British thermal units (pound-degrees Fahr.) per minute when the difference between the temperatures of its opposite faces is 1° F., find the conductivity on the Centigrade system in C.G.S. units.* (1 lb. = 453·6 grm.; 1 in. = 2·54 cm.)

$$\text{H} = 7 \cdot 5 \times \tfrac{5}{9} \times 453 \cdot 6 \text{ units}; \ \tau_1 - \tau_2 = \tfrac{5}{9}°; \ l = 2 \cdot 54$$

$$\text{A} = (12 \times 2 \cdot 54)^2 \quad ;$$

$$\text{whence } k = \cdot 155.$$

5. *If we take v in the equation of an ideal gas, $pv = \text{R}\text{T}$, to be the volume of m grammes of a gas of which the molecular weight is m, show that R is the same* for all gases, and find its value in C.G.S. units, given that the density of hydrogen at 0° C. and a pressure of 1 megadyne per sq. cm. is ·0896 grm. per litre.

6. A cylindrical solid rod is heated from 0° C. to 100° C. If the linear expansion of the rod is 9×10^{-6}, what is the percentage increase of the surface of the rod?

7. *A glass flask 1 litre in capacity is closed by a cork through which passes* a capillary tube. The flask contains some mercury, and is filled up with water, which occupies also part of the tube, the temperature being 0° C. What must be the volume of the mercury in order that, when the temperature rises, the motion of the liquid in the capillary tube may indicate the change of volume of the water? Coefficient of expansion of mercury ·00018, and of glass (linear) ·000009.

8. A piece of sulphur weighs 50 grm. in air, and has a volume of 25 c.cm. when the temperature is 17° C. and pressure 74 cm. What is its true weight, the density of air being ·00129 (grm. per c.cm.) at 0° and 76 cm., the coefficient of expansion of air being $\frac{1}{273}$, and the density of the brass weights 8.

The difference between the upthrusts is the weight of 18·75 c.cm. of air, which at 17° and 74 cm. is ·0221 grm.

9. A glass bulb of 20 c.cm. capacity at 0° C. containing dry hydrogen at the atmospheric pressure of 760 mm. of mercury is heated to 100° C. at constant pressure. Find the volume of gas expelled measured at 0° C. and 760 mm. pressure, if the coefficient of expansion of hydrogen is $\frac{1}{273}$ and that of glass $\frac{1}{38700}$.

10. If 1 grm. of water expands by ·0918 c.cm. on freezing and evolves 80 calories, calculate the specific heat of a substance, 10 grm. of which, when introduced into a Bunsen's calorimeter at a temperature of 100° C., produce a contraction of 70 c.mm.

11. In a determination of vapour density by Victor Meyer's method the following quantities were obtained: weight of liquid, ·119 grm.; volume of air driven off, 38 c.cm.; temperature of air, 15° C.; height of mercury in measuring tube above free surface, 5 cm.; height of barometer, 75 cm. Calculate the vapour density of the substance used.

12. A jacketed vessel contains a liquid in which a spiral of wire is immersed. An E.M.F. of 20 volts is applied to the ends of the spiral, and a current of 2 amperes passes through it. 5 grm. of the liquid are boiled away every minute after steady boiling has begun. What is the latent heat of vaporization of the liquid?

13. A cylinder of 10 litres internal volume contains gas at a pressure of 100 atmospheres, which is allowed to escape slowly into the air, the temperature of the cylinder remaining constant. Find the heat absorbed.

14. Explain how the fusing-points of bodies under pressure depend upon their volumes in the liquid and in the solid state. What relation have these changes to the dynamical theory of heat, and what conclusions may be drawn as to the relation between the latent heat of fusion and the temperature of fusion?

15. With what velocity must a mass of coal containing 75 per cent of carbon be moving, in order that its kinetic energy may equal the energy developed by its combustion?

16. A certain pendulum is 35·024 in. long at 0° C., and its time of vibration is ·9047 sec.; at 40° C. its time of vibration is ·9050 sec. Find the coefficient of expansion of the metal.

17. Find the rate at which a jet of hydrogen must burn in air that the energy developed may be equivalent to 1 horse-power.

18. A mass of air at atmospheric pressure is compressed by the action of an engine, and is heated thereby. It is afterwards cooled down to its original temperature before compression, and is then expanded while doing work. When it again arrives at the pressure of the atmosphere it is intensely cold, and may be used for refrigerating purposes. Explain these results according to the principles of thermodynamics. Why is it an advantage to cause the air to do work while expanding?

19. The Lake of Geneva has an area of 240 sq. miles. Suppose it to be frozen to a depth of 6 in. What is the weight of the ice? How much work was done on the atmosphere during the congelation? How many units of heat were given out in freezing? How many tons of coal would melt the ice?

[1 c. ft. of water weighs 62·5 lb. 1 c. ft. of water makes 1·089 c. ft. of ice. The combustion of 1 lb. of coal yields 8600 pound-degrees (Centigrade). Standard atmospheric pressure = 2116 lb. per sq. ft.]

20. How many kilogram-metres of work must be done to decompose 1 kg.